REACTIONS OF BUTYLAMINES
OVER ALUMINA CATALYSTS

By

DAVID S. COBBLEDICK

UNIVERSITY OF FLORIDA
January, 1957

ACKNOWLEDGMENT

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

SECTION I

INTRODUCTION

The rates of a great many chemical reactions have
been found to be influenced by solid surfaces, which are
said to catalyze the reaction. This investigation is con-
cerned with the course of a particular group of related
reactions--those in the transformation of primary and
secondary amines--at the surface of aluminum oxide cata-
lysts, and with the manner in which the course and rate
of reaction are related to the structure of the solid.

The general picture of the function of a solid
catalyst is that only by virtue of the formation of a
chemisorbed layer are one or more reactants brought into
a more highly reactive state than that possible in the gas
phase under the same conditions of temperature and pressure.
The effective catalyst unit may be thought of as a small
group of neighbor or near neighbor atoms, whose configura-
tion or properties are such that they exert the requisite
forces on the reactant, assisting the breaking of some bonds,
and--by orienting the reactants on the surface so that the
atoms required for the reaction products are in close
proximity--the formation of other bonds.

1

The surface of the solid is obviously a very important factor in the effectiveness of the catalyst since the reaction takes place at the solid-gas interface. Several features of the surface nature of a solid catalyst which are important are the surface area, pore structure, lattice spacing on the surface, and unsatisfied valence forces. The area of surface exposed to reactant molecules and the quantity of reactant molecules converted to products show a direct relationship. The influence of the surface area is, however, often masked by other factors such as pore size and lattice spacing on the surface. Small pores appear to have different catalytic properties, due to their control of the partial pressure of the reactant molecules in the inner pore recesses. Reactant molecules partially trapped in the small pores may pass through a series of reactions while reactant molecules on the surface pass through only one or two reactions. The lattice spacing or the geometry of the surface of a solid and the unsatisfied valence forces determine the forces of attraction of different catalyst atoms for the various parts of the reactant molecules. As such forces only operate over short distances, the interaction is largely determined by the relative spacing of surface and reactant atoms. The surface may also show so large a variation in properties from

point to point that only a small fraction of the total surface is catalytically active.

This study was undertaken with the purpose of determining the products of the reaction of n-butylamine over alumina at elevated temperatures, of finding how changes in the structure and surface area of the alumina influence the activity of the alumina as a catalyst, and of studying the kinetics of the reaction of n-butylamine over alumina. Because of the absence of water in the reaction, it was thought to be a suitable reaction for studying the effects of the amount of water in the surface of the alumina on the activity of the alumina as a catalyst.

The catalytic reaction of n-butylamine over alumina has not previously been extensively studied. The first step in the investigation was the study of the path of the reaction in order to establish what significance the observed quantities of the various products obtained in the reaction have as a measure of catalytic activity.

The properties of the alumina were varied by thermal treatment at 500° and 800° both in a vacuum and in the presence of water vapor.[a] The form of the solid used was

---

[a]All temperatures in this and the following sections are given on the Centigrade scale, unless otherwise designated.

identified by means of X-ray diffraction measurements.

REVIEW OF PREVIOUS WORK

A. The Catalyst--Surface Area, Structure, Activity, and Activation of Alumina

The variation in surface area of alumina with increasing temperatures of activation has been studied by Krieger (13), Boreskov, Dzis'ko, and Borisova (1), Boreskov, Dzis'ko, Borisova, and Krasnopol'skaya (2), and Brey and Krieger (4). It was found that for temperatures of activation not exceeding 600° the surface area is essentially constant. Further increase of the temperature of activation to 750° decreases the area by nearly 15 per cent while heating to 950° further decreases the area by nearly 40 per cent. Boreskov, Dzis'ko, Borisova, and Krasnopol'skaya attributed the decrease in area for temperatures of activation above 600° to the disappearance of narrow pores.

Changes in the crystal structure of alumina with increasing temperatures of activation have been studied by means of X-ray diffraction measurements by Brey and Krieger (4), and Boreskov, Dzis'ko, Borisova, and Krasnopol'skaya (2). It was found that samples activated between 500° and 900° consist of gamma alumina. Samples activated at 1000°

5

are partially converted to the alpha form while higher tem-
peratures of activation result in larger conversions to the
alpha form.

The variation of the activity of alumina with changes
in surface area and with increasing temperatures of activa-
tion has been studied. One of these studies was that by
Brey and Krieger (4), who measured the activity of samples
of alumina activated by heating in a vacuum and in the
presence of water vapor at temperatures between 500° and
1000° for the dehydration of ethanol at reaction tempera-
tures of 350° and 500°. The surface area of the samples
of alumina was determined by absorption of nitrogen at
liquid nitrogen temperatures. They found that both total
activity and specific activity decrease as the temperature
increases above 600°. Heating in the presence of water
vapor induces an additional loss of area and activity as
compared with heating in a vacuum, but specific activity
of the surface is nearly independent of water vapor.

Another investigation of the variation of activity
with activation conditions is that of Boreskov, Dzis'ko,
Borisova, and Krasnopol'skaya (2), who compared the activ-
ity and surface area of samples of alumina activated at
450°, 600°, 800°, 1000°, and 1200° for the dehydration of
ethanol. They found that activation at higher temperatures
decreases the total activity; however, the specific activity

increases even after heat treatment at 1000°. After heat treatment at 1200°, the specific activity decreases markedly and the catalyst becomes mainly dehydrogenating. These results indicate that the specific activity of gamma alumina does not depend on heat treatment up to 1000°. The apparent rise is due to the disappearance of small pores which were inaccessible to reactant molecules but which were accessible to the molecules used for determining the surface area.

The variation of activity with crystallite size and with surface area has been studied by Rubinshtein, Vasseberg, and Pribytova (16). Three forms of alumina of different grain size were prepared and their activity for the dehydration of ethanol measured. The linear dimensions of the crystallites were less than 35, 35, and 51.4 $\overset{\circ}{A}$ and the coarsest form was found to be the most active. The surface areas determined by the B. E. T. method by adsorption of methanol vapor at 25° were the same for all three forms. The surface areas determined by the adsorption of C_6H_{12} were quite different and were found to be directly proportional to the crystallite size. It was concluded from these results that portions of the surface, especially in fine pores, which are easily accessible to methanol, are not accessible to the larger C_6H_{12} molecules. This shows that the surface area of a catalyst is a function of the size of the molecules with which that surface area is

measured, and that the lower activity of the finer forms of
the alumina is due to the presence of finer micropores
which are useless for the dehydration of ethanol.

B. The Reaction--Deamination of
Butylamine over Alumina

The only literature reference to the reaction of
butylamine over alumina is a Dutch patent (15) on the pro-
duction of secondary aliphatic or cycloaliphatic amines from
primary aliphatic or cycloaliphatic amines. According to
the abstract of this patent, liquid butylamine was mixed
with ammonia in the mole ratio 2:1 and passed over alumina
at 350° and a total pressure of 20 kg./sq. cm. at a rate
of 100 cc. liquid butylamine/liter of catalyst/hour. It
was found that for each 100 moles of butylamine, 34 moles
were converted into 2-aminobutane, three moles into butene
and ammonia, three moles into other products of dissociation,
and 60 moles remained unchanged. The alumina used for this
reaction was activated at 500° for three hours.

The decomposition of ethylamine over kaolin at 500°,
700°, and 1000°, and the decomposition of propylamine over
kaolin at 700° have been studied by Upson and Sands (18)
but only in a qualitative manner. It was found that the
chief products formed by the decomposition of ethylamine
at 500° are ammonia, hydrogen cyanide, ethylene, and a

substance which is probably acetonitrile, together with smaller quantities of hydrogen and nitrogen. At 700° more ethylene is formed and no hydrogen cyanide. At 1000° the chief products were the elements, although traces of ethylene and probably acetonitrile are formed. Propylamine at 700° gives chiefly a nitrile, ammonia, carbon and hydrocarbons, together with small quantities of hydrogen cyanide and the elements.

The reactions in the systems methanol-ammonia, ethanol-ammonia, butanol-ammonia, and 2-amino-2-methyl-1-propanol over alumina have been studied. The reactions in the systems alcohol-ammonia result in the formation of mono-, di-, and trialkylamines and are of interest due to this fact.

The first work done on the reactions in the systems alcohol-ammonia was that by Sabatier and Mailhe (17). It was found that a mixture of mono-, di-, and trialkylamines is formed by passing the vapor of an alcohol with ammonia over a variety of catalysts, including alumina, at elevated temperatures.

Brown and Reid (6) studied the alkylation of ammonia by methyl, ethyl, n-propyl, and n-butyl alcohols by passing their vapors with ammonia over a variety of catalysts, one of which was alumina, between 300° and 500°. It was found that a mixture of mono-, di-, and trialkylamines is formed.

Butyl alcohol and ammonia in the ratio of 1:1.5 moles re-
spectively were passed over alumina at 360° at a rate of
one mole of the alcohol per 5.6 hours and it was found
that 6.55 moles of amines were produced for every 100 moles
of butyl alcohol passed over the catalyst.

Dorrell (9) studied the reaction in the system
ethanol-ammonia over alumina, varying such factors as
temperature, time of contact, and the ratio of alcohol to
ammonia. Change of these variables was compared to the
per cent conversion to ethylamine. It was found that in-
creasing the temperature of the catalyst bed from 239° to
293° results in an increase in per cent conversion to
ethylamine while increasing the temperature from 293° to
344° results in a decrease. Increasing the time of con-
tact does not, under all conditions, increase the per cent
conversion to ethylamine as expected, and Dorrell concluded
that the most probable cause of this is the decomposition of
the ethylamine. Increasing the ratio of alcohol to ammonia
results in an increase in the quantities of di- and tri-
ethylamines formed.

Breiner and Gandillon (3) studied the reaction in
the system methanol-ammonia over alumina in order to obtain
amines in a simple and more direct manner and to learn more
about contact catalysis in dehydration. A mixture of mono-,
di-, and trimethylamines was obtained under all experimental

conditions, and, where the total yield of amines was small, monomethylamine was the main product. A stepwise path was indicated due to the rapid conversion of dimethylamine to trimethylamine when the ammonia was replaced by monomethylamine or dimethylamine. The optimum temperature was about 460°. Increasing the ratio of alcohol to ammonia and decreasing the time of contact resulted in decreased yields of amines.

Egly and Smith (10) made an extensive study of the effects of operating variables on the reaction in the system methanol-ammonia over alumina to form a mixture of mono-, di-, and trimethylamines. The effects of changing pressure, temperature, and space velocity upon the per cent conversion of methanol and ammonia to mono-, di-, and trimethylamines were determined.

Egly and Smith found that as the temperature is increased at a constant space velocity the per cent conversion to monomethylamine increases, passes through a maximum, and then decreases. As the per cent conversion to monomethylamine decreases, the per cent conversion to trimethylamine increases. Further increase of the temperature at constant space velocity causes the per cent conversion to trimethylamine to pass through a maximum and then decrease. This result was attributed to cracking of the trimethylamine molecules. Decreasing the space velocity or increasing

the contact time at a constant temperature was found to give
similar results. As the space velocity is decreased, the
per cent conversion to monomethylamine either reaches a
maximum or passes through a maximum and then decreases, de-
pending on the temperature. At temperatures where the per
cent conversion to monomethylamine passes through a maximum
and then decreases, the per cent conversion to trimethyl-
amine increases.

Clarke, O'Leary, and Karabinos (8) studied the re-
action of 2-amino-2-methyl-1-propanol over alumina at 300°.
The chief products formed were ammonia, isobutylene, iso-
butylidene imine, isobutylamine, diisobutylamine, and
2,2,5,5-tetramethyl-3,6-dihydroxypiperazine, the dimer of
2-amino-2-methyl-1-propanol. A mechanism for the reaction
was proposed which indicated that deamination, amination,
dehydrogenation, and hydrogenation occur as well as de-
hydration.

EXPERIMENTAL METHODS

A. Catalytic Reaction Runs

1. Apparatus

The arrangement of the apparatus used in the butylamine and dibutylamine decomposition runs is shown in Figure 1. The feed material was contained in a 500 ml. separatory funnel, A, from which the liquid was fed by means of a finely grooved stopcock, B, through a section of the feed system, C, which was maintained at a temperature of 30.0° by means of a water jacket. The liquid from the feed system passed through the flowmeter, D, which was maintained at 30.0° by means of a water jacket, and into the delivery tube, from which the liquid was fed into the first arm of the reaction tube.

The reaction tube, E, was made from 17 mm. heavy-walled Pyrex glass tubing and was immersed in the salt bath, G. The reaction tube was bent into the shape of a double "U" in order to fit into the salt bath. The first "U" portion was packed with glass helices to preheat the amine to reaction temperature. The first arm of the second "U" portion served as the reaction chamber. This arm was 16.5 cm.

FIGURE I - APPARATUS
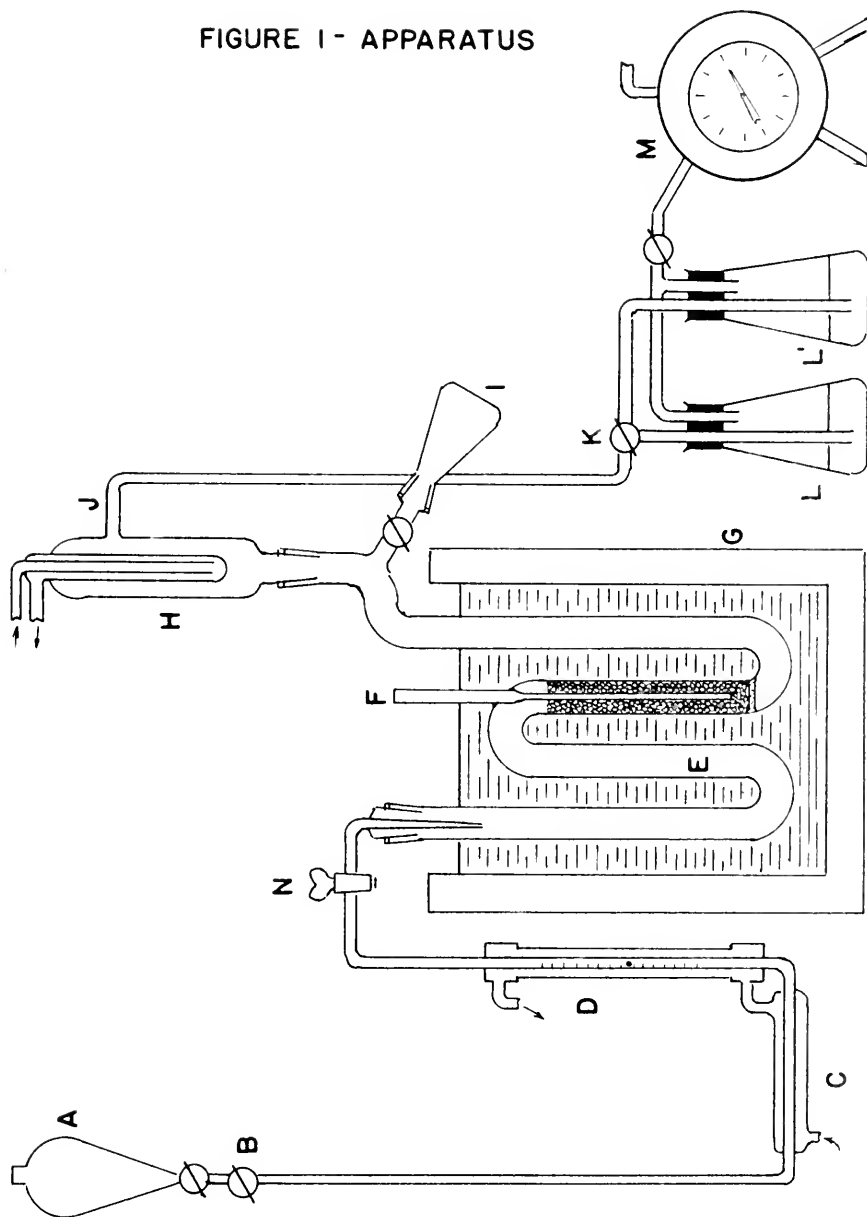
in length and was equipped with a thermocouple well, F, and a porous porcelain plug which supported the catalyst bed.

The salt bath, G, was made from a section of quarter-inch wall iron tubing 13 in. in length and 5 in. in diameter. The salt bath was supported by an iron panel box the dimensions of which are given in Figure 2. A flat cover plate was welded to the bottom of the iron tube and a large square plate with a 5 in. circular hole was welded to the top of the tube. This flange had a rim attached to its edge so that it rested snugly on top of the box. The salt mixture was composed of 53 per cent potassium nitrate, 17 per cent sodium nitrate, and 30 per cent lithium nitrate.

The temperature of the salt bath was controlled by connecting a chromel-alumel thermocouple immersed in the bath with a model 234 Wheelco Proportioning Capacitrol. This instrument, connected in series with the heater, automatically controlled the temperature of the salt bath to any desired temperature setting of the instrument within a range of 2°. The thermocouple and lead wires were enclosed in a Pyrex protecting sheath in order to prevent deterioration of the couple.

The temperature in the reaction chamber was read by connecting a chromel-alumel thermocouple inserted in the thermocouple well, F, with the model 234 Wheelco Proportioning Capacitrol. The thermocouple terminals of this

FIGURE 2 - SALT BATH
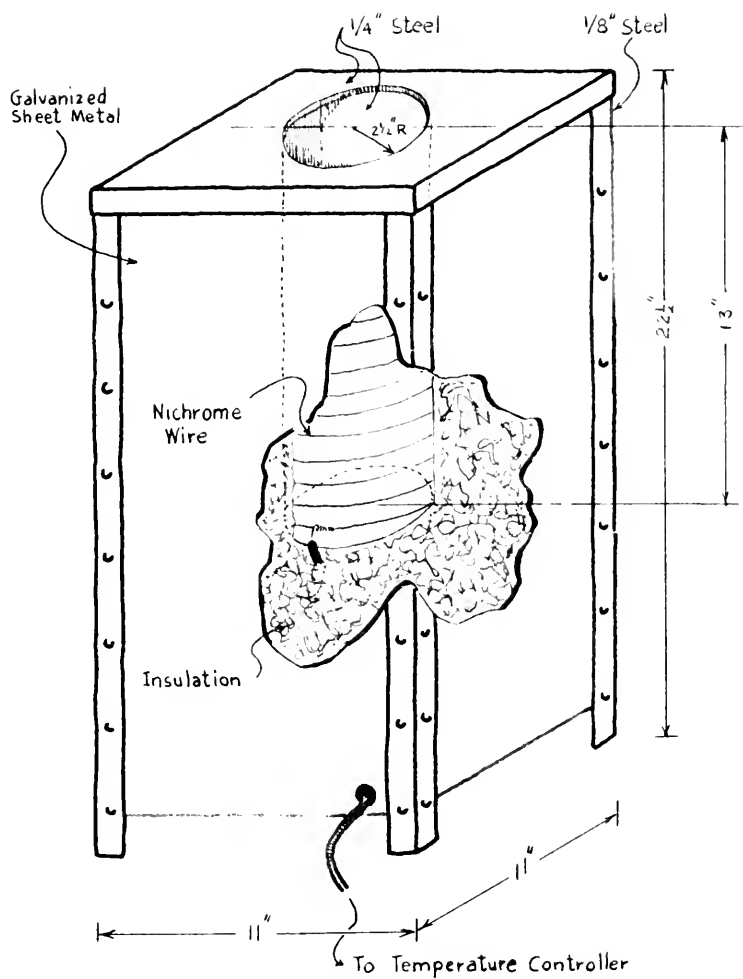
instrument were provided with a throw switch which made it
possible to connect the leads from either the couple in the
bath or that in the well.

The delivery tube fed the liquid into the first
"U" portion of the reaction tube where it was vaporized,
brought to temperature, and passed through the reaction
chamber. The vapor issuing from the second "U" portion of
the reaction tube passed over the condenser, H, which was
maintained at a temperature of $0°$, where the condensible
products were separated and collected in the receiver, I.
The gaseous products passed through the side arm, J, and
were led to a two-way stopcock, K, which could be adjusted
to divert the gas stream to receiver L or L' from which it
passed through a wet-test meter, M, into a sampling bulb.
The sampling bulb was connected to a Fisher Gas Analyzer,
No. 10-600-4.

2. Calibration of Flowmeter

The flowmeter used for the runs was an Emil Greiner
flowmeter, Cat. No. G-9142. It was calibrated for butyl-
amine and dibutylamine at $30.0°$ by passing the amines
through the flow system at various flowmeter readings and
collecting the samples in volumetric flasks. Because of
the volatility of the butylamine, the samples were collected
at $0°$ and the volume was then corrected to $30.0°$ by applying

the correction for cubical expansion. The volumes at 30.0°
were divided by the time of flow in minutes to give the
flowrate in milliliters per minute of the liquid. The
range of feed rates obtainable, using both sapphire and
steel rotors, was from about 0.434 to 1.97 ml. of liquid
per minute. Reproducible results were obtained as long as
the flow system was filled with liquid but the reproduci-
bility of feed rates after emptying the flow system and
cleaning it was not good. In order to avoid uncertainty
in the feed rate, the flowmeter was recalibrated before
every run or set of runs.

3. Materials

The butylamine and dibutylamine were Eastman Or-
ganic Chemicals, White Label Grade. These materials were
found to contain small quantities of water and were dried
over potassium hydroxide and distilled before being used.

The catalyst material used was taken from one large
quantity of Alcoa Activated Alumina, grade F-10, obtained
in the form of granules of 8 to 14 mesh size. The catalyst
batches were treated before use by heating in vacuum or in
the presence of water vapor. The alumina was placed in a
quartz tube and heated in a furnace with heat control and
temperature measurement like that used for the salt bath.

4. Reaction Run Procedure

Twenty-five grams of activated alumina was placed in the reaction chamber of the reaction tube. The salt in the bath was melted, the reaction tube placed in the molten salt bath, and the bath heated 10° above the temperature at which it was desired to make a run. The delivery tube and condenser, H, were connected to the reaction tube, and the three-way stopcock, N, in the delivery tube was adjusted so that the flow system was shut off from the reaction tube. A mechanical vacuum pump was attached to the side arm of the condenser and the reaction tube evacuated and filled with argon by means of the three-way stopcock, N. The salt bath was then allowed to cool to the desired temperature, the feed system filled with the amine, and the side arm of the condenser attached to receiver L. The stopcock, N, was opened to the reaction tube, and the amine passed through the reaction tube over the activated catalyst.

The first portion of the products was passed through receiver L until the system had come to thermal equilibrium. This was done in order that liquid hold-up in the reaction chamber might come to a constant value, and to permit the water in the wet-test meter to come to equilibrium with the exit gas. Stopcock H was then adjusted to pass the gaseous products through receiver L', and

receiver I was replaced by a graduated receiver. The
products were collected for a timed period, and simul-
taneously the volume of gas was measured by the wet-test
meter and a sample was withdrawn for analysis. The products
in receivers I and L' were then analyzed by the procedures
described in Section 6 below. At the conclusion of each
run the volume of condensible products and the volume of
gas measured by the wet-test meter were recorded, and the
reaction tube evacuated and filled with argon by a proce-
dure similar to that used before starting the initial run.

In many cases several runs were made without dis-
connecting the system. During such a series, either the
feed rate or the temperature was changed between runs.
After the last run of the set, the reaction tube was
evacuated and filled with argon as described above. The
delivery tube and condenser were then disconnected from
the reaction tube and the latter removed from the salt
bath and flushed out with argon while cooling.

5. Separation and Identification of Products

Seven preliminary runs were made with butylamine
over a sample of alumina, which had been activated at 500°
in a vacuum, in order to find out what products were formed
in the reaction. These runs were made between 415° and 448°

at a reciprocal space velocity of 11.2.[a] In these runs
the receivers, L and L', were traps cooled in a Dry Ice-
acetone mixture, rather than containers for sulfuric acid
solutions as in the standard procedure adopted in later
work.

An infrared spectrum was obtained for the conden-
sible products collected in the receiver, I, and then these
products were separated as well as possible by fractional
distillation. The infrared spectrum of the first fraction
between 77° and 78° was identical with that of the feed
material. After removal of the unreacted butylamine, the
distillate was collected in 5° fractions up to 180°. The
infrared spectrum of the fraction between 115° and 120°
indicated that this fraction contained butyronitrile. The
infrared spectrum of the fraction between 155° and 160°
indicated that this fraction contained dibutylamine and
N-butylidenebutylamine. Infrared spectra were run on the
pure compounds for comparison. Butyronitrile was prepared
according to the procedure of Jeffery and Vogel (12). N-
butylidenebutylamine was prepared according to the procedure
of Campbell, Sommers, and Campbell (7). In addition to the

---

[a]The reciprocal space velocity was computed by
dividing the total volume of the catalyst bed by the volume
of gas at standard conditions equivalent to the amount of
amine fed per second.

unreacted butylamine, dibutylamine, N-butylidenebutylamine, and butyronitrile were identified. The absorptions of these compounds, together with the absorption of butylamine, accounted for the spectrum of the products before separation.

The spectrum of the residue from the distillation showed, in addition to traces of dibutylamine and N-butylidenebutylamine, another compound or compounds which did not appear in the spectrum of the condensible products before distillation. According to Emerson, Hess, and Uhle (11) pure N-butylidenebutylamine dimerizes when refluxed between 140° and 150°. The infrared spectrum of N-butylidenebutylamine which had been refluxed for two hours was almost identical with the spectrum of the residue. This accounts for the presence of the additional compound or compounds not found in the spectrum of the condensible products before distillation.

The products collected in the Dry Ice traps separated into two distinct layers. The infrared spectrum of the products collected during the first run indicated the presence of ammonia and unsaturated hydrocarbons. The volatile products obtained from the third run were passed, in turn, through a saturated solution of sodium chloride, a drying tower, and Dry Ice traps. An infrared spectrum of the products collected in the Dry Ice traps indicated that the unsaturated hydrocarbons were probably 1-butene and

ethylene. The ethylene appeared to be present only in trace quantities. The mixture in the traps was brominated and 1,2-dibromobutane was separated and identified by its boiling point and refractive index. The dibromo- derivative of ethylene could not be separated.

The saturated solution of sodium chloride was made acidic by the addition of 6M HCl, evaporated almost to dryness, and cooled down to room temperature, and a saturated solution of sodium hydroxide added until the solution was basic. This solution was heated to 95° with constant stirring and the gas evolved passed, in turn, through an ice trap, a drying tower, and Dry Ice traps. The infrared spectrum of the products collected in the Dry Ice traps was identical with that of ammonia.

The gaseous products obtained from the seventh run were passed first through concentrated sulfuric acid and then into the Dry Ice traps. No liquid condensed in the Dry Ice but, after warming the traps and forcing the gas into an infrared gas cell, a spectrum was obtained which was identical with the spectrum of ethylene.

In addition to ammonia, 1-butene, and ethylene, which accounted for the spectrum of the gaseous products from the traps before separation, hydrogen and methane were also identified by Orsat analysis of the gases collected in the sample bulb. The separation and identification

of methane is described in Section 6 below.

Three preliminary runs were made with dibutylamine
over a sample of alumina which had been activated at 500°
in a vacuum. These runs were made between 415° and 438° at
a reciprocal space velocity of 11.2. The procedure and ap-
paratus used for these runs were the same as those described
for the preliminary runs with butylamine.

The products from these runs were separated and
identified by procedures similar to those used for separating
and identifying the products from the butylamine runs. The
same compounds were identified and no additional compounds
were found.

6. Analytical Methods

(a) Analysis of condensed products.--Two infrared
cells were cleaned and calibrated by measurement of their
interference patterns. The cell lengths were found to be
0.0270 and 0.0542 mm., and the former will be referred to
as the "standard" cell.

The infrared spectra of butylamine, dibutylamine,
N-butylidenebutylamine, and butyronitrile were run and the
wavelengths suitable for use in quantitative analysis were
chosen. These wavelengths were chosen such that the opti-
cal density of only one of the components of the reaction
mixture was large and those of the other components were

small. The wavelengths and optical density of each compound with the standard cell filled with the pure liquid are recorded in Table 1.

TABLE 1

WAVELENGTHS AND OPTICAL DENSITIES

	Butyro-nitrile	N-butylidene-butylamine	Butyl-amine	Dibutyl-amine
4.40μ	0.571[a]	0.017	0.010	0.018
5.96μ	0.027	2.000[a]	0.120	0.016
6.23μ	0.023	0.050	0.410[a]	0.025
8.87μ	0.025	0.235	0.235	1.160[a]

[a]Characteristic band

Eight synthetic mixtures of known weights, four containing butylamine, dibutylamine, and N-butylidenebutylamine, and four containing all four compounds, were prepared and analyzed. The results are tabulated in the appendix.

The fraction of the total volume of each of the above compounds in the synthetic mixtures was calculated by means of a series of successive approximations from values in the table above by the following procedure. It was found that, because of a shift in the base line, 0.011 and 0.014 had to be added to the optical densities at 4.40 and 6.23μ respectively. The optical densities at these

wavelengths after adding the correction will be referred to
as the "corrected" optical densities.

The corrected optical density at 4.40μ was divided
by the optical density of pure butyronitrile at 4.40μ and
an approximate value of the fraction of the total volume
which was butyronitrile was obtained. This value was then
multiplied by the optical density of pure butyronitrile at
5.96, 6.23, and 8.87μ and these values subtracted from
the optical density at these wavelengths. The optical
density at 5.96μ, minus the value due to butyronitrile,
was divided by the optical density of pure N-butylidene-
butylamine at 5.96μ and an approximate value of the
fraction of the total volume which was N-butylidenebutyl-
amine obtained. This value was then multiplied by the
optical densities of pure N-butylidenebutylamine at 4.40,
6.23, and 8.87μ and these values subtracted from the
optical density at these wavelengths. The corrected op-
tical density at 6.23μ, minus the values due to butyro-
nitrile and N-butylidenebutylamine, was divided by the
optical density of pure butylamine at 6.23μ and an approxi-
mate value of the total volume which was butylamine obtained.
This value was then multiplied by optical densities of pure
butylamine at 4.40, 5.96, and 8.87μ and these values sub-
tracted from the optical densities at these wavelengths.
The optical density at 8.87μ, minus the values due to

butyronitrile, N-butylidenebutylamine, and butylamine, was
divided by the optical density of pure dibutylamine at
8.87μ and an approximate value of the total volume which
was dibutylamine obtained. This value was then multiplied
by the optical densities of pure dibutylamine at 4.40,
5.96, and 6.23μ and these values subtracted from the op-
tical densities at these wavelengths.

The second approximation was calculated as follows.
The corrected optical density at 4.40μ minus the values
due to N-butylidenebutylamine, butylamine, and dibutylamine,
was divided by the optical density of pure butyronitrile at
4.40μ and a new approximation of the fraction of the total
volume which was butyronitrile obtained. This value was then
multiplied by the optical density of pure butyronitrile at
5.96, 6.23, and 8.87μ and these values subtracted from the
optical density at these wavelengths. The optical density
at 5.96μ, minus the new value due to butyronitrile and
the values due to butylamine and dibutylamine, was divided
by the optical density of pure N-butylidenebutylamine at
5.96μ and the same procedure followed as used previously.
These successive approximations were repeated until dupli-
cate results were obtained. Three successive approxima-
tions were usually found to be sufficient.

In the absence of butyronitrile, the fraction of
the total volume of each of the compounds in the synthetic

mixtures was calculated by the same procedure as used previously except the successive approximations began with the optical density at 5.96μ, characteristic of N-butylidenebutylamine.

The number of milliliters of each of these compounds was calculated from the total volume and the fraction of the total volume of the compound. The weights and numbers of moles of the compounds were calculated from the numbers of milliliters, densities, and molecular weights of the compounds.

(b) Analysis of gaseous products.--The gaseous products were analyzed by first removing the ammonia and any condensible products swept over during a run from the gases by absorption in a known volume of a sulfuric acid solution of known strength contained in receiver L'. The sulfuric acid solution was then back titrated with sodium hydroxide and the moles of base collected during a run in receiver L' calculated. The gaseous products, after the removal of ammonia and any condensible products, consisted of 1-butene, ethylene, and hydrogen, and were analyzed by the following procedure.

The per cent by volume of each of the gaseous products was determined by analyzing a 100 ml. sample of the gases in an Orsat type gas analyzer. 1-Butene and ethylene were determined by absorption in an 87 per cent

solution of sulfuric acid and a 22 per cent solution of
sulfuric acid containing 57 gms. of mercuric sulfate per
200 gms. of 22 per cent sulfuric acid, respectively (5 and
14). Hydrogen was then determined by passing the gases
over copper oxide at 300° and noting the decrease in volume
due to formation of water. The difference between the
initial volume and the volume remaining after the removal
of hydrogen was found to be the per cent by volume of
methane. Methane was identified by oxidizing the saturated
hydrocarbon left, after the removal of hydrogen, by passing
a mixture of the hydrocarbon and oxygen over a hot platinum
wire. From the decrease in volume because of the formation
of water and the volume of carbon dioxide produced, the
saturated hydrocarbon was identified.

The individual volumes of 1-butene, ethylene, hydro-
gen, and methane were calculated from their per cent by
volume and the volume of the gaseous products which passed
through the wet-test meter. The numbers of moles of 1-
butene, ethylene, hydrogen, and methane were calculated,
assuming ideality, from their volumes, temperature, and
pressure.

(c) Calculations based on extended analysis.--Eight
runs were made with butylamine over a sample of alumina
which had been activated at 500° in a vacuum and the products
analyzed and material balances obtained. These runs were

made between $415°$ and $430°$ at several flow rates.

The procedures used for analyzing the condensible products collected in receiver I and the gaseous products, after removal of ammonia and any condensible products, were those previously described in parts (a) and (b) respectively. The base collected in receiver L' consisted of ammonia and any condensible products which were swept over during a run. Butylamine is the only condensible product which has an appreciable vapor pressure at $0°$, the temperature at which the condenser, H, was maintained, and as a result it was assumed that butylamine was the only condensible product swept over. The number of moles of butylamine swept over was calculated, assuming ideality, by the following procedure. The number of moles of gaseous products which passed through the wet-test meter was calculated from the volume, temperature, and pressure. The number of moles of base collected in receiver L' plus the number of moles of gaseous products passed through the wet-test meter was taken as the number of moles of gas passing through condenser H. This figure was multiplied by the vapor pressure of butylamine at $0°$ and then divided by the barometric pressure to obtain the number of moles of butylamine swept over. The number of moles of ammonia collected in the trap, L', was calculated by subtracting the moles of butylamine swept over from the moles of base collected.

The total number of moles of butylamine unreacted during the butylamine runs or the total number of moles of butylamine produced during the dibutylamine runs consists of the sum of the number of moles collected in receivers I and L'.

The number of moles of ammonia dissolved in the condensible products during a run was calculated by the following procedure. The total moles of butylamine, dibutylamine, N-butylidenebutylamine, and butyronitrile and the moles of ammonia collected in receiver L' were added together and subtracted from the moles of butylamine passed over the catalyst during a run. This difference was assumed to be ammonia dissolved in the condensible products since no nitrogen was found in the gaseous products. The weight of ammonia in the condensible products was calculated from the number of moles dissolved and its molecular weight.

The amount of 1-butene dissolved in the condensible products during a run was calculated by the following procedure. The number of milliliters of condensible products collected in receiver I was multiplied by the density of the condensible products and the total weight obtained. The weights of the butylamine, dibutylamine, N-butylidenebutylamine, butyronitrile, and ammonia present in the condensible products were subtracted from the total weight and the

difference assumed to be 1-butene dissolved in the conden-
sible products.

The material balances obtained for these eight runs
were found to be very satisfactory and the results are tabu-
lated in the appendix.

(d) Analysis based on material balances.--Using the
data from these same eight runs, it was found that satis-
factory material balances substantially equivalent could be
obtained without carrying out the gas analysis. The calcu-
lations of the amounts of products were then modified as
follows.

The condensible products collected in receiver I
were analyzed by the procedure previously described in
part (a). The total number of moles of butylamine un-
reacted or produced during a run was calculated by the
procedure previously described in part (c). The total
number of moles of ammonia produced during a run was cal-
culated by a nitrogen balance by the following procedure.
The numbers of moles of butylamine, dibutylamine, N-butyl-
idenebutylamine, and butyronitrile were added together and
subtracted from the moles of butylamine passed over the
catalyst during a run; the difference is the number of
moles of ammonia produced.

The total number of moles of 1-butene produced
during a run was calculated by a "butyl radical" balance

by the following procedure. The total moles of butylamine, the moles of dibutylamine and N-butylidene multiplied by two, and the moles of butyronitrile were added together and subtracted from the moles of butylamine passed over the catalyst during a run; the difference is the number of moles of 1-butene produced.

The number of moles of hydrogen produced during a run was calculated by multiplying the moles of butyronitrile by two and adding to this the moles of N-butylidenebutyl-amine.

B. Activation and Measurement of X-ray Diffraction of the Catalyst

The samples of alumina were activated by heat treatment at 500° and 800° for about 48 hours either in a vacuum or in the presence of water vapor. The alumina was placed in a quartz tube, heated the prescribed length of time in a pot furnace, and then bottled.

The form of the activated alumina was investigated by means of a North American X-ray diffraction recording spectrophotometer. The radiation used was produced by a copper target with the X-ray tube operating at 35 kilovolts with a current of 15 milliamperes. The samples, ground to pass through a 200 mesh screen, were mounted in a thin film on a plastic holder.

RESULTS

A. Presentation of Data

The operating conditions and results of the reaction runs of butylamine and dibutylamine are presented in Tables 2 and 3 respectively. Catalyst A and B are the catalysts activated at 500° and 800°, respectively. Some of the figures in the tables require explanation. Column (9) is a reciprocal space velocity, computed by dividing the total volume of the catalyst bed by the volume of gas at standard conditions equivalent to the amount of amine fed per second.

Column (14) gives the weight of the condensible products collected in receiver I during a run; this weight was calculated by multiplying the volume of the condensible products by the density. Column (20) gives the number of moles of gaseous products which passed through the wet-test meter during a run. Column (21) gives the total number of moles of gaseous products, which is the sum of the moles of base collected in receiver L' and the moles of gaseous products which passed through the wet-test meter during a run. The other figures in the tables are explained in the section on analytical methods and reference to this section

can be made for an explanation.

TABLE 2

REACTION RUNS WITH BUTYLAMINE

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Run No.	Catalyst	Temp. in Salt Bath	Temp. in React. Cham.	Time of Run, Min.	Feed Vol. Ml.	Feed Wt., Grams	Feed, Moles Amine	$\dfrac{1}{GSSV}$
9	A-1	425	418	30.0	22.5	16.5	0.226	11.2
10	A-1	418	413	30.0	22.5	16.5	0.226	11.2
11	A-1	417	414	30.0	22.5	16.5	0.226	11.2
12	A-1	430	423	30.0	22.5	16.5	0.226	11.2
13	A-1	422	417	30.0	22.5	16.5	0.226	11.2
14	A-1	422	418	25.0	22.5	16.5	0.226	9.3
15	A-1	418	414	30.0	22.5	16.5	0.226	11.2
16		430	433	20.0	15.0	11.0	0.151	11.2
17	A-2	430	424	30.0	22.5	16.5	0.226	11.2
18	A-2	425	420	30.0	22.5	16.5	0.226	11.2
19	A-2	420	417	30.0	22.5	16.5	0.226	11.2
20	A-2	415	412	30.0	22.5	16.5	0.226	11.2
21	A-2	429	423	30.0	22.5	16.5	0.226	11.2
22	A-2	410	408	30.0	22.5	16.5	0.226	11.2
24	A-2	400	399	30.0	22.5	16.5	0.226	11.2
25	A-2	405	403	30.0	22.5	16.5	0.226	11.2
26	A-2	391	392	30.0	22.5	16.5	0.226	11.2
27	A-2	415	412	24.0	22.8	16.7	0.229	8.8
28	A-2	415	412	20.0	23.0	16.9	0.231	7.3
29	A-2	396	397	30.0	22.5	16.5	0.226	11.2
30	A-2	380	382	30.0	22.5	16.5	0.226	11.2
31	A-2	415	412	18.0	26.1	19.2	0.263	5.6
32	A-2	415	412	14.0	25.4	18.6	0.256	4.6
33	A-2	415	412	12.0	27.1	19.9	0.273	3.7
34	A-2	400	399	24.0	22.8	16.7	0.229	8.8
35	A-2	400	399	21.0	24.2	17.7	0.243	7.3
36	A-2	400	399	18.0	26.1	19.2	0.263	5.6
37	A-2	400	399	12.0	25.0	18.3	0.251	4.0
38	B-1	430	424	30.0	22.5	16.5	0.226	11.2
39	B-1	425	421	30.0	22.5	16.5	0.226	11.2
40	B-1	420	417	30.0	22.5	16.5	0.226	11.2
41	B-1	416	413	30.0	22.5	16.5	0.226	11.2
42	B-1	429	423	30.0	22.5	16.5	0.226	11.2

TABLE 2 (Continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Run No.	Catalyst	Temp. in Salt Bath	Temp. in React. Cham.	Time of Run, Min.	Feed Vol. Ml.	Feed Wt., Grams	Feed, Moles Amine	$\dfrac{1}{GSSV}$
50	B-2	424	418	30.0	25.8	18.9	0.259	10.0
51	B-2	418	413	25.0	21.5	15.8	0.216	10.0
52	B-2	413	409	25.0	21.5	15.8	0.216	10.0
53	B-2	407	404	25.0	21.5	15.8	0.216	10.0
54	B-2	401	398	25.0	21.5	15.8	0.216	10.0

	(10)	(11)	(12)	(13)	(14)
Run No.	Condensible Products--Weight in Grams				
	Butyl-amine	Dibutyl-amine	N-Butylidene-butylamine	Butyro-nitrile	Total Liquid
9	3.05	3.18	0.94	3.02	11.72
10	3.41	4.19	1.12	2.42	12.50
11	4.34	4.79	1.31	1.29	12.38
12	3.54	2.65	0.96	2.43	10.50
13	4.20	3.75	1.20	1.68	11.38
14	4.17	4.40	1.35	1.42	11.80
15	3.98	4.20	1.18	1.58	11.55
16	11.00	0.00	0.00	0.00	11.00
17	3.39	2.28	0.82	2.34	10.53
18	3.62	3.23	1.01	1.98	11.23
19	3.86	4.10	1.14	1.60	11.87
20	4.20	4.77	1.21	1.26	12.48
21	3.36	2.43	0.91	2.22	10.60
22	4.26	5.31	1.23	1.09	12.70
24	5.04	5.82	1.27	0.61	13.14
25	4.50	5.58	1.25	0.84	12.96
26	7.17	5.45	1.22	0.42	14.15
27	4.22	5.26	1.30	1.31	13.00
28	4.60	5.74	1.54	1.10	14.03
29	5.76	5.78	1.28	0.58	13.80
30	10.70	3.70	0.78	0.00	15.32
31	6.92	6.07	1.85	0.88	15.80
32	7.72	5.57	1.82	0.65	15.76
33	9.66	5.03	1.76	0.50	16.84
34	6.82	5.15	1.30	0.48	14.00
35	8.82	4.79	1.34	0.42	15.40
36	11.37	4.44	1.34	0.39	17.50
37	12.84	2.86	0.94	0.32	16.58

TABLE 2 (Continued)

	(10)	(11)	(12)	(13)	(14)
Run No.	Condensible Products--Weight in Grams				
	Butyl-amine	Dibutyl-amine	N-Butylidene-butylamine	Butyro-nitrile	Total Liquid
38	3.59	3.45	1.01	2.76	11.68
39	3.98	3.64	1.11	2.24	11.94
40	4.10	4.49	1.25	1.82	12.65
41	4.30	4.96	1.31	1.53	12.84
42	3.64	3.18	1.05	2.67	11.77
50	4.45	3.92	1.11	2.32	13.80
51	3.98	4.04	1.02	1.45	11.77
52	4.35	4.70	1.09	1.12	12.46
53	4.63	5.29	1.16	0.75	12.84
54	5.50	5.62	1.20	0.49	13.26

	(15)	(16)	(17)	(18)	(19)
Run No.	Condensible		Products--Moles		Total Base in L'
	Butyl-amine	Dibutyl-amine	N-Butylidene-butylamine	Butyro-nitrile	
9	0.0418	0.0246	0.0074	0.0437	0.0980
10	0.0467	0.0324	0.0089	0.0351	0.0936
11	0.0593	0.0371	0.0103	0.0187	0.0989
12	0.0485	0.0205	0.0076	0.0351	0.1124
13	0.0575	0.0290	0.0095	0.0244	0.1042
14	0.0572	0.0340	0.0106	0.0206	0.1008
15	0.0542	0.0325	0.0093	0.0228	0.0996
16	0.151	0.0000	0.0000	0.0000	0.0000
17	0.0465	0.0177	0.0065	0.0340	0.1130
18	0.0495	0.0250	0.0080	0.0296	0.1090
19	0.0528	0.0318	0.0090	0.0232	0.1052
20	0.0575	0.0369	0.0096	0.0182	0.1020
21	0.0460	0.0188	0.0072	0.0321	0.1147
22	0.0582	0.0411	0.0097	0.0158	0.0959
24	0.0690	0.0450	0.0100	0.0089	0.0800
25	0.0617	0.0447	0.0098	0.0122	0.0892
26	0.0982	0.0422	0.0096	0.0061	0.0604
27	0.0577	0.0407	0.0102	0.0190	0.0954
28	0.0628	0.0445	0.0121	0.0160	0.0951
29	0.0789	0.0447	0.0101	0.0084	0.0790
30	0.1464	0.0287	0.0061	0.0000	0.0380
31	0.0947	0.0469	0.0146	0.0128	0.0904
32	0.1057	0.0431	0.0143	0.0094	0.0776
33	0.1322	0.0390	0.0138	0.0072	0.0700

TABLE 2 (Continued)

Run No.	(15) Butyl-amine	(16) Dibutyl-amine	(17) N-Butylidene-butylamine	(18) Butyro-nitrile	(19) Total Base in L'
		Condensible	Products--Moles		Total
34	0.0933	0.0399	0.0102	0.0071	0.0680
35	0.1205	0.0371	0.0105	0.0061	0.0606
36	0.1557	0.0344	0.0106	0.0056	0.0527
37	0.1760	0.0222	0.0074	0.0046	0.0352
38	0.0492	0.0236	0.0079	0.0400	0.1006
39	0.0544	0.0282	0.0087	0.0327	0.0982
40	0.0552	0.0348	0.0099	0.0264	0.0954
41	0.0588	0.0390	0.0103	0.0222	0.0920
42	0.0498	0.0246	0.0082	0.0387	0.1006
50	0.0608	0.0304	0.0088	0.0336	0.1220
51	0.0545	0.0313	0.0081	0.0210	0.0976
52	0.0580	0.0364	0.0086	0.0162	0.0927
53	0.0633	0.0410	0.0091	0.0109	0.0867
54	0.0753	0.0435	0.0094	0.0071	0.0790

Run No.	(20) Moles of Gaseous Prods.	(21) Total Moles of Gaseous Prods.	(22) Butyl-amine in L'	(23) Ammonia in L'	(24) Total Butyl-amine	(25) Ammonia in Liquid Prods.
9	0.157	0.254	0.0104	0.0876	0.0522	0.010
10	0.122	0.216	0.0089	0.0847	0.0552	0.009
11	0.089	0.188	0.0077	0.0912	0.0670	0.002
12	0.154	0.266	0.0109	0.1015	0.0594	0.002
13	0.115	0.219	0.0090	0.0952	0.0665	0.003
14	0.097	0.198	0.0081	0.0927	0.0653	0.003
15	0.102	0.202	0.0082	0.0914	0.0624	0.008
16	0.000	0.000	0.0000	0.0000	0.1510	0.000
17	0.156	0.269	0.0110	0.1020	0.0575	0.008
18	0.129	0.238	0.0098	0.0992	0.0593	0.006
19	0.105	0.210	0.0086	0.0966	0.0614	0.003
20	0.089	0.191	0.0078	0.0941	0.0653	0.002
21	0.151	0.266	0.0109	0.1037	0.0569	0.007
22	0.071	0.167	0.0068	0.0891	0.0650	0.005
24	0.043	0.123	0.0050	0.0750	0.0764	0.013
25	0.058	0.128	0.0053	0.0839	0.0670	0.008

TABLE 2 (Continued)

	(20)	(21)	(22)	(23)	(24)	(25)
Run No.	Moles of Gaseous Prods.	Total Moles of Gaseous Prods.	Butyl-amine in L'	Ammonia in L'	Total Butyl-amine	Ammonia in Liquid Prods.
26	0.020	0.080	0.0032	0.0572	0.1014	0.009
27	0.081	0.176	0.0072	0.0882	0.0649	0.006
28	0.070	0.165	0.0068	0.0883	0.0696	0.001
29	0.040	0.083	0.0034	0.0756	0.0823	0.005
30	0.015	0.053	0.0022	0.0358	0.1486	0.004
31	0.052	0.143	0.0059	0.0845	0.1006	0.004
32	0.042	0.120	0.0048	0.0728	0.1105	0.006
33	0.035	0.105	0.0043	0.0657	0.1362	0.011
34	0.034	0.102	0.0042	0.0638	0.0975	0.010
35	0.028	0.089	0.0036	0.0570	0.1247	0.008
36	0.025	0.083	0.0034	0.0543	0.1591	0.000
37	0.016	0.052	0.0021	0.0331	0.1781	0.006
38	0.152	0.253	0.0104	0.0902	0.0596	0.005
39	0.127	0.225	0.0092	0.0890	0.0636	0.004
40	0.103	0.198	0.0081	0.0873	0.0633	0.004
41	0.087	0.179	0.0073	0.0847	0.0660	0.004
42	0.146	0.247	0.0101	0.0905	0.0599	0.004
50	0.143	0.265	0.0109	0.1111	0.0717	0.003
51	.094	0.192	0.0079	0.0897	0.0624	0.003
52	0.075	0.168	0.0069	0.0858	0.0649	0.004
53	0.056	0.143	0.0059	0.0808	0.0692	0.005
54	0.040	0.119	0.0049	0.0741	0.0802	0.002

TABLE 2 (Continued)

Run No.	(26) Total Ammonia Prod.	(27) 1-Butene in Liquid Prods.	(28) 1-Butene Prod.	(29) Hydro-gen Prod.	(30) Conversion Fraction of Feed Butyl-amine	(31) Dibutyl-amine
9	0.098	0.0239	0.066	0.095	0.231	0.218
10	0.094	0.0214	0.053	0.079	0.244	0.287
11	0.093	0.0112	0.046	0.048	0.296	0.328
12	0.104	0.0157	0.075	0.078	0.263	0.182
13	0.098	0.0082	0.058	0.058	0.294	0.256
14	0.096	0.0073	0.051	0.052	0.289	0.301
15	0.099	0.0084	0.057	0.055	0.276	0.288
16	0.000	0.000	0.000	0.000	1.000	0.000
17	0.110	0.0281	0.086	0.074	0.254	0.157
18	0.105	0.0228	0.072	0.065	0.263	0.221
19	0.100	0.0197	0.060	0.055	0.272	0.281
20	0.096	0.0198	0.050	0.046	0.287	0.327
21	0.111	0.0296	0.085	0.071	0.252	0.166
22	0.094	0.0126	0.044	0.041	0.288	0.363
24	0.088	0.0032	0.033	0.028	0.327	0.398
25	0.092	0.0101	0.038	0.034	0.296	0.395
26	0.066	0.0096	0.015	0.022	0.449	0.373
27	0.094	0.0149	0.043	0.048	0.283	0.356
28	0.089	0.0187	0.032	0.044	0.301	0.385
29	0.081	0.0076	0.026	0.027	0.364	0.395
30	0.042	0.0004	0.008	0.006	0.658	0.254
31	0.088	0.000	0.027	0.040	0.383	0.357
32	0.079	0.000	0.021	0.033	0.432	0.336
33	0.077	0.000	0.024	0.028	0.488	0.288
34	0.074	0.0014	0.024	0.024	0.426	0.349
35	0.065	0.000	0.017	0.023	0.503	0.305
36	0.054	0.000	0.008	0.022	0.603	0.262
37	0.039	0.000	0.009	0.017	0.710	0.177
38	0.095	0.0143	0.063	0.088	0.263	0.209
39	0.093	0.0087	0.056	0.073	0.281	0.250
40	0.091	0.0164	0.047	0.063	0.280	0.304
41	0.089	0.0116	0.039	0.054	0.292	0.345
42	0.094	0.0205	0.061	0.086	0.265	0.217
50	0.114	0.0337	0.075	0.076	0.276	0.235
51	0.093	0.0216	0.054	0.050	0.289	0.290
52	0.090	0.0202	0.046	0.041	0.300	0.338
53	0.092	0.0169	0.036	0.031	0.321	0.380
54	0.076	0.0075	0.023	0.024	0.371	0.403

TABLE 2 (Continued)

Run No.	(32)	(33)	(34)	(35)	(36)
	Conversion Fraction of Feed			Partial Pressure	
	N-Butylidene-butylamine	Butyro-nitrile	1-Butene	Butyl-amine	Dibutyl-amine
9	0.066	0.193	0.292	0.135	0.064
10	0.079	0.155	0.234	0.154	0.090
11	0.091	0.091	0.203	0.209	0.116
12	0.067	0.155	0.334	0.156	0.054
13	0.084	0.108	0.257	0.194	0.085
14	0.094	0.091	0.225	0.196	0.102
15	0.082	0.101	0.252	0.185	0.096
16	0.000	0.000	0.000	1.000	0.000
17	0.058	0.151	0.380	0.149	0.046
18	0.071	0.221	0.318	0.164	0.069
19	0.080	0.102	0.265	0.180	0.093
20	0.085	0.080	0.221	0.203	0.114
21	0.064	0.142	0.376	0.149	0.049
22	0.086	0.070	0.194	0.209	0.132
24	0.088	0.039	0.146	0.258	0.157
25	0.087	0.054	0.168	0.225	0.150
26	0.085	0.027	0.066	0.387	0.161
27	0.089	0.083	0.198	0.203	0.127
28	0.105	0.069	0.138	0.227	0.145
29	0.089	0.037	0.115	0.294	0.160
30	0.054	0.000	0.034	0.622	0.120
31	0.111	0.049	0.103	0.305	0.142
32	0.112	0.037	0.086	0.356	0.139
33	0.101	0.026	0.088	0.419	0.120
34	0.089	0.031	0.105	0.352	0.144
35	0.086	0.025	0.070	0.440	0.131
36	0.080	0.021	0.034	0.542	0.117
37	0.059	0.018	0.036	0.643	0.080
38	0.070	0.177	0.279	0.158	0.063
39	0.077	0.145	0.248	0.178	0.079
40	0.087	0.117	0.206	0.189	0.104
41	0.091	0.098	0.174	0.206	0.122
42	0.073	0.171	0.270	0.162	0.066
50	0.068	0.130	0.290	0.175	0.074
51	0.075	0.097	0.250	0.195	0.098
52	0.080	0.075	0.208	0.214	0.120
53	0.084	0.051	0.167	0.240	0.142
54	0.087	0.033	0.106	0.305	0.165

TABLE 2 (Continued)

Run No.	(37) N-Butylidene-butylamine	(38) Butyro-nitrile	(39) Ammonia	(40) 1-Butene	(41) Hydrogen
			Partial Pressure		
9	0.019	0.113	0.235	0.171	0.245
10	0.025	0.098	0.263	0.148	0.221
11	0.032	0.058	0.291	0.144	0.150
12	0.020	0.092	0.274	0.198	0.205
13	0.028	0.071	0.285	0.169	0.169
14	0.032	0.062	0.291	0.155	0.158
15	0.028	0.068	0.293	0.168	0.163
16	0.000	0.000	0.000	0.000	0.000
17	0.017	0.088	0.285	0.223	0.193
18	0.022	0.079	0.289	0.198	0.180
19	0.026	0.068	0.293	0.176	0.163
20	0.030	0.056	0.298	0.155	0.143
21	0.019	0.084	0.291	0.223	0.186
22	0.031	0.051	0.302	0.141	0.132
24	0.035	0.031	0.306	0.115	0.102
25	0.033	0.041	0.308	0.128	0.114
26	0.037	0.023	0.252	0.057	0.084
27	0.032	0.059	0.294	0.134	0.150
28	0.039	0.052	0.290	0.104	0.143
29	0.036	0.030	0.289	0.093	0.096
30	0.026	0.000	0.176	0.033	0.025
31	0.044	0.039	0.267	0.082	0.121
32	0.046	0.030	0.255	0.068	0.106
33	0.042	0.022	0.237	0.074	0.086
34	0.037	0.026	0.267	0.087	0.088
35	0.037	0.022	0.230	0.060	0.080
36	0.036	0.019	0.194	0.027	0.075
37	0.027	0.016	0.141	0.032	0.060
38	0.021	0.106	0.252	0.167	0.234
39	0.024	0.092	0.251	0.157	0.208
40	0.030	0.079	0.272	0.140	0.188
41	0.032	0.069	0.278	0.122	0.171
42	0.022	0.105	0.254	0.165	0.226
50	0.021	0.082	0.278	0.183	0.185
51	0.025	0.066	0.291	0.169	0.156
52	0.028	0.053	0.297	0.152	0.135
53	0.032	0.038	0.318	0.125	0.107
54	0.036	0.027	0.288	0.087	0.090

TABLE 2 (Continued)

(1) Run No.	(2) Catalyst	(3) Temp. in Salt Bath	(4) Temp. in React. Cham.	(5) Time of Run, Min.	(6) Feed Vol., Ml.	(7) Feed Wt., Grams	(8) Feed, Moles Amine	(9) $\frac{1}{GSSV}$
55	B-2	429	422	25.0	21.5	15.8	0.216	10.0
61	B-1	410	408	30.0	22.5	16.5	0.226	11.2
65	B-2	430	423	30.0	20.7	15.2	0.208	12.1
66	B-2	423	417	30.0	20.7	15.2	0.208	12.1
67	B-2	417	413	30.0	20.7	15.2	0.208	12.1
68	B-2	411	408	30.0	20.7	15.2	0.208	12.1
69	B-2	429	422	30.0	20.7	15.2	0.208	12.1
70	B-2	405	403	30.0	20.9	15.3	0.210	12.1
71	B-2	399	398	30.0	20.9	15.3	0.210	12.1
72	B-2	393	393	30.0	20.9	15.3	0.210	12.1
73	B-2	383	384	30.0	20.9	15.3	0.210	12.1
75	B-2	429	423	30.0	20.8	15.3	0.209	12.1
76	A-2	429	423	30.0	22.9	16.8	0.230	11.0
77	A-2	429	423	30.0	22.9	16.8	0.230	11.0
78	A-4	425	421	30.0	22.5	16.5	0.226	11.2
79	A-4	425	421	30.0	22.5	16.5	0.226	11.2
93	B-2	415	412	30.0	20.3	14.9	0.204	12.4
94	B-2	415	412	25.0	20.9	15.3	0.210	10.0
95	B-2	415	412	20.0	22.3	16.4	0.224	7.5
96	B-2	402	400	30.0	20.3	14.9	0.204	12.4
97	B-2	402	400	25.0	20.9	15.3	0.210	10.0
98	B-2	402	400	20.0	22.3	16.4	0.224	7.5
99	B-2	415	412	18.0	25.8	18.9	0.259	5.8
100	B-2	415	412	14.0	27.1	19.9	0.272	4.3
101	B-2	415	412	9.0	25.5	18.7	0.256	3.0
102	B-2	402	400	18.0	25.8	18.9	0.259	5.8
103	B-2	402	400	14.0	27.1	19.9	0.272	4.3
104	B-2	402	400	9.0	25.5	18.7	0.256	3.0
105	B-3	415	413	30.0	21.2	15.6	0.213	11.9
106	B-3	415	413	26.0	21.7	15.9	0.218	10.0
107	B-3	415	413	21.0	22.4	16.4	0.225	7.9
108	B-3	415	413	18.0	25.8	18.9	0.259	5.8
109	B-3	415	413	14.0	27.7	20.3	0.278	4.3
110	B-3	415	413	9.0	26.6	19.5	0.267	3.0

44

TABLE 2 (Continued)

	(10)	(11)	(12)	(13)	(14)
Run No.	Butyl-amine	Dibutyl-amine	N-Butylidene-butylamine	Butyro-nitrile	Total Liquid
55	3.42	2.81	0.86	2.29	10.84
61	4.12	5.92	1.47	1.59	13.50
65	2.87	2.20	0.80	3.53	10.54
66	2.99	3.14	0.94	2.55	10.94
67	3.25	4.10	1.10	1.89	11.50
68	3.67	4.88	1.20	1.37	12.02
69	2.82	2.35	0.78	3.28	10.62
70	4.55	5.58	1.32	0.94	12.75
71	5.28	5.74	1.36	0.58	13.20
72	6.59	5.32	1.29	0.41	13.83
73	10.39	3.38	0.84	0.00	14.48
75	2.81	2.20	1.06	2.79	10.13
76	3.09	2.42	0.85	2.84	10.54
77	3.08	2.56	0.89	2.86	10.54
78	3.35	2.90	0.95	2.16	11.30
79	3.60	3.35	1.06	2.27	11.63
93	3.90	4.20	1.21	1.40	11.50
94	4.00	4.48	1.29	1.18	11.78
95	4.90	4.86	1.52	0.98	12.70
96	5.08	4.95	1.28	0.72	12.68
97	6.05	5.27	1.35	0.55	13.12
98	7.58	4.74	1.38	0.47	13.94
99	8.18	5.28	1.88	0.73	15.88
100	10.65	4.24	1.81	0.65	17.56
101	12.73	2.89	1.37	0.00	17.14
102	11.92	3.47	1.23	0.54	17.18
103	15.44	2.59	1.00	0.00	18.60
104	16.22	1.19	0.61	0.00	17.90
105	5.08	4.87	1.50	0.75	12.78
106	5.42	4.94	1.56	0.57	13.05
107	6.57	5.17	1.71	0.48	13.95
108	9.23	4.93	1.81	0.43	16.67
109	12.54	4.08	1.71	0.00	18.60
110	14.42	2.68	1.24	0.00	18.25

TABLE 2 (Continued)

	(15)	(16)	(17)	(18)	(19)
Run No.	Condensible Products--Moles				Total Base in L'
	Butyl-amine	Dibutyl-amine	N-Butylidene-butylamine	Butyro-nitrile	
55	0.0468	0.0218	0.0068	0.0332	0.1030
61	0.0563	0.0458	0.0116	0.0231	0.0868
65	0.0392	0.0170	0.0063	0.0512	0.0932
66	0.0409	0.0243	0.0074	0.0369	0.0904
67	0.0445	0.0317	0.0086	0.0273	0.0880
68	0.0503	0.0378	0.0095	0.0198	0.0863
69	0.0385	0.0182	0.0062	0.0475	0.0940
70	0.0625	0.0432	0.0104	0.0135	0.0837
71	0.0724	0.0445	0.0107	0.0084	0.0745
72	0.0903	0.0412	0.0101	0.0059	0.0610
73	0.1422	0.0262	0.0064	0.000	0.0344
75	0.0385	0.0170	0.0084	0.0404	0.0948
76	0.0413	0.0187	0.0067	0.0411	0.1093
77	0.0421	0.0198	0.0070	0.0414	0.1058
78	0.0461	0.0225	0.0074	0.0313	0.1201
79	0.0492	0.0259	0.0083	0.0329	0.1121
93	0.0533	0.0325	0.0096	0.0203	0.0882
94	0.0547	0.0347	0.0101	0.0172	0.0841
95	0.0672	0.0376	0.0119	0.0142	0.0812
96	0.0697	0.0383	0.0101	0.0104	0.0735
97	0.0828	0.0408	0.0106	0.0080	0.0672
98	0.1035	0.0367	0.0108	0.0068	0.0596
99	0.1120	0.0409	0.0148	0.0106	0.0804
100	0.1458	0.0328	0.0143	0.0094	0.0680
101	0.1740	0.0224	0.0108	0.000	0.0455
102	0.1633	0.0269	0.0097	0.0079	0.0476
103	0.2115	0.0201	0.0078	0.000	0.0340
104	0.2220	0.0092	0.0048	0.000	0.0202
105	0.0695	0.0377	0.0118	0.0108	0.0798
106	0.0742	0.0383	0.0123	0.0083	0.0826
107	0.0900	0.0399	0.0134	0.0070	0.0763
108	0.1262	0.0382	0.0142	0.0063	0.0713
109	0.1718	0.0316	0.0134	0.000	0.0576
110	0.1972	0.0208	0.0098	0.000	0.0347

TABLE 2 (Continued)

Run No.	(20) Moles of Gaseous Prods.	(21) Total Moles of Gaseous Prods.	(22) Butyl- amine in L'	(23) Ammonia in L'	(24) Total Butyl- amine	(25) Ammonia in Liquid Prods.
55	0.139	0.242	0.0099	0.0930	0.0567	0.005
61	0.080	0.167	0.0068	0.0800	0.0631	0.003
65	0.172	0.265	0.0109	0.0823	0.0501	0.001
66	0.135	0.225	0.0092	0.0812	0.0501	0.008
67	0.106	0.194	0.0079	0.0800	0.0524	0.008
68	0.080	0.166	0.0068	0.0795	0.0571	0.004
69	0.164	0.258	0.0106	0.0834	0.0492	0.004
70	0.057	0.141	0.0058	0.0780	0.0683	0.000
71	0.047	0.122	0.0050	0.0695	0.0774	0.000
72	0.003	0.064	0.0026	0.0584	0.0929	0.002
73	0.002	0.036	0.0015	0.0329	0.1437	0.000
75	0.150	0.245	0.0101	0.0847	0.0486	0.010
76	0.163	0.272	0.0112	0.0980	0.0525	0.013
77	0.162	0.268	0.0110	0.0948	0.0531	0.014
78	0.148	0.268	0.0110	0.1090	0.0571	0.000
79	0.140	0.262	0.0107	0.1014	0.0599	0.000
93	0.088	0.176	0.0072	0.0810	0.0605	0.000
94	0.076	0.160	0.0066	0.0775	0.0613	0.009
95	0.062	0.143	0.0059	0.0753	0.0731	0.012
96	0.044	0.118	0.0048	0.0687	0.0745	0.002
97	0.037	0.104	0.0043	0.0630	0.0871	0.000
98	0.030	0.090	0.0037	0.0560	0.1072	0.006
99	0.048	0.128	0.0052	0.0752	0.1172	0.001
100	0.038	0.106	0.0044	0.0636	0.1502	0.001
101	0.023	0.069	0.0028	0.0427	0.1768	0.003
102	0.023	0.071	0.0029	0.0447	0.1662	0.003
103	0.017	0.051	0.0021	0.0319	0.2136	0.000
104	0.011	0.031	0.0013	0.0198	0.2233	0.000
105	0.054	0.134	0.0055	0.0743	0.0750	0.003
106	0.049	0.132	0.0054	0.0772	0.0796	0.002
107	0.040	0.116	0.0048	0.0715	0.0948	0.000
108	0.035	0.106	0.0044	0.0669	0.1306	0.000
109	0.025	0.083	0.0034	0.0542	0.1752	0.003
110	0.018	0.053	0.0022	0.0325	0.1994	0.004

TABLE 2 (Continued)

	(26)	(27)	(28)	(29)	(30)	(31)
Run No.	Total Ammonia Prod.	1-Butene in Liquid Prods.	1-Butene Prod.	Hydrogen Prod.	Conversion Fraction of Feed	
					Butyl-amine	Dibutyl-amine
55	0.098	0.0244	0.069	0.073	0.262	0.202
61	0.083	0.0070	0.025	0.058	0.279	0.405
65	0.083	0.0200	0.060	0.109	0.241	0.163
66	0.089	0.0210	0.058	0.081	0.241	0.234
67	0.088	0.0184	0.048	0.063	0.252	0.305
68	0.084	0.0150	0.036	0.049	0.274	0.363
69	0.087	0.0128	0.062	0.101	0.237	0.175
70	0.078	0.0066	0.021	0.037	0.325	0.411
71	0.074	0.0045	0.014	0.028	0.369	0.423
72	0.060	0.0037	0.009	0.022	0.442	0.392
73	0.033	0.000	0.000	0.007	0.685	0.249
75	0.095	0.0100	0.069	0.089	0.232	0.163
76	0.111	0.0239	0.085	0.089	0.228	0.163
77	0.109	0.0205	0.082	0.090	0.230	0.172
78	0.108	0.0346	0.078	0.070	0.252	0.199
79	0.104	0.0068	0.065	0.074	0.265	0.229
93	0.081	0.0014	0.039	0.050	0.296	0.318
94	0.086	0.0091	0.042	0.044	0.292	0.330
95	0.087	0.0025	0.038	0.040	0.326	0.332
96	0.071	0.0110	0.022	0.031	0.365	0.375
97	0.063	0.000	0.012	0.027	0.415	0.389
98	0.062	0.000	0.015	0.024	0.479	0.328
99	0.076	0.000	0.020	0.036	0.452	0.316
100	0.065	0.0034	0.018	0.033	0.552	0.241
101	0.046	0.0016	0.013	0.011	0.692	0.175
102	0.048	0.000	0.012	0.026	0.642	0.208
103	0.032	0.000	0.003	0.008	0.785	0.148
104	0.019	0.000	0.005	0.005	0.873	0.072
105	0.077	0.0094	0.028	0.033	0.352	0.354
106	0.079	0.0094	0.029	0.029	0.365	0.351
107	0.072	0.000	0.018	0.027	0.421	0.355
108	0.067	0.0048	0.018	0.027	0.505	0.295
109	0.057	0.0039	0.013	0.013	0.630	0.227
110	0.036	0.000	0.006	0.010	0.747	0.155

TABLE 2 (Continued)

Run No.	(32)	(33)	(34)	(35)	(36)
	Conversion Fraction of Feed			Partial Pressure	
	N-Butylidene-butylamine	Butyro-nitrile	1-Butene	Butyl-amine	Dibutyl-amine
55	0.063	0.154	0.319	0.158	0.061
61	0.107	0.102	0.110	0.204	0.148
65	0.061	0.245	0.288	0.133	0.045
66	0.071	0.171	0.279	0.144	0.070
67	0.082	0.131	0.231	0.164	0.099
68	0.091	0.095	0.173	0.195	0.129
69	0.060	0.226	0.298	0.133	0.049
70	0.099	0.064	0.100	0.251	0.159
71	0.102	0.040	0.067	0.301	0.173
72	0.096	0.026	0.043	0.386	0.171
73	0.061	0.000	0.000	0.665	0.121
75	0.080	0.193	0.330	0.132	0.046
76	0.058	0.178	0.370	0.130	0.046
77	0.061	0.180	0.357	0.132	0.049
78	0.066	0.138	0.345	0.153	0.060
79	0.073	0.145	0.287	0.162	0.070
93	0.094	0.099	0.191	0.206	0.111
94	0.096	0.084	0.200	0.208	0.117
95	0.105	0.064	0.169	0.242	0.125
96	0.099	0.051	0.108	0.290	0.149
97	0.101	0.038	0.057	0.351	0.164
98	0.097	0.030	0.066	0.407	0.140
99	0.114	0.041	0.077	0.373	0.130
100	0.105	0.035	0.066	0.465	0.102
101	0.084	0.000	0.051	0.632	0.080
102	0.075	0.030	0.046	0.562	0.091
103	0.058	0.000	0.011	0.752	0.071
104	0.038	0.000	0.020	0.839	0.035
105	0.111	0.051	0.131	0.275	0.138
106	0.113	0.038	0.135	0.288	0.139
107	0.119	0.032	0.080	0.349	0.147
108	0.110	0.024	0.069	0.434	0.127
109	0.096	0.000	0.047	0.577	0.104
110	0.074	0.000	0.024	0.707	0.074

TABLE 2 (Continued)

Run No.	(37) N-Butylidene-butylamine	(38) Butyro-nitrile	(39) Ammonia	(40) 1-Butene	(41) Hydrogen
		Partial Pressure			
55	0.061	0.093	0.274	0.193	0.204
61	0.038	0.075	0.268	0.081	0.187
65	0.017	0.136	0.221	0.160	0.289
66	0.021	0.106	0.256	0.167	0.234
67	0.027	0.086	0.276	0.150	0.198
68	0.032	0.068	0.287	0.123	0.167
69	0.017	0.128	0.235	0.167	0.272
70	0.038	0.050	0.287	0.077	0.136
71	0.042	0.033	0.288	0.054	0.107
72	0.042	0.024	0.249	0.037	0.091
73	0.030	0.000	0.153	0.000	0.030
75	0.023	0.110	0.259	0.188	0.243
76	0.017	0.102	0.275	0.210	0.220
77	0.017	0.103	0.271	0.204	0.224
78	0.020	0.084	0.289	0.209	0.187
79	0.022	0.089	0.281	0.176	0.200
93	0.031	0.069	0.276	0.133	0.171
94	0.034	0.058	0.291	0.142	0.149
95	0.039	0.047	0.282	0.126	0.132
96	0.039	0.040	0.276	0.086	0.121
97	0.043	0.032	0.254	0.048	0.109
98	0.041	0.026	0.236	0.057	0.093
99	0.047	0.034	0.242	0.064	0.111
100	0.044	0.029	0.201	0.056	0.102
101	0.039	0.000	0.164	0.046	0.039
102	0.033	0.027	0.162	0.040	0.086
103	0.027	0.000	0.113	0.011	0.027
104	0.018	0.000	0.071	0.019	0.018
105	0.043	0.040	0.282	0.103	0.121
106	0.045	0.030	0.286	0.105	0.105
107	0.049	0.026	0.265	0.066	0.100
108	0.047	0.021	0.223	0.060	0.090
109	0.044	0.000	0.188	0.043	0.044
110	0.035	0.000	0.128	0.021	0.035

TABLE 3

REACTION RUNS WITH DIBUTYLAMINE

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Run No.	Catalyst	Temp. in Salt Bath	Temp. in React. Cham.	Time of Run, Min.	Feed Vol., Ml.	Feed Wt., Grams	Feed, Moles Amine	$\frac{1}{GSSV}$
62	A-3	422	410	20.0	25.0	18.8	0.146	11.6
63	A-3	429	414	20.0	25.0	18.8	0.146	11.6
64	A-3	432	415	20.0	25.0	18.8	0.146	11.6
80	A-3	425	413	25.0	26.8	20.0	0.156	13.5
81	A-3	425	413	20.0	25.9	19.5	0.151	11.2
82	A-3	425	414	15.0	25.9	19.5	0.151	8.4
83	A-3	425	414	12.0	27.3	20.5	0.159	6.4
84	A-3	411	403	25.0	23.4	17.6	0.136	15.5
85	A-3	411	403	20.0	24.0	18.1	0.140	12.0
86	A-3	411	404	15.0	25.0	18.8	0.146	8.7
87	A-3	411	405	12.0	27.3	20.5	0.159	6.4
88	A-3	425		18.0	25.7	19.3	0.150	4.0
89	A-3	425		12.0	27.3	20.5	0.159	2.5
90	A-3	411		18.0	25.7	19.3	0.150	4.0
91	A-3	411		12.0	27.3	20.5	0.159	2.5
92		430	432	20.0	24.0	18.1	0.140	12.0

(10)	(11)	(12)	(13)	(14)
Run No.		Condensible Products--Weight in Grams		
	Butyl-amine	Dibutyl-amine	N-Butylidene-butylamine	Butyro-nitrile	Total Liquid

Run No.	Butyl-amine	Dibutyl-amine	N-Butylidene-butylamine	Butyro-nitrile	Total Liquid
62	1.65	7.37	1.90	1.34	15.22
63	1.57	6.18	1.86	1.78	14.40
64	2.14	4.22	1.58	2.58	14.20
80	2.38	5.84	2.12	2.62	16.25
81	2.14	6.25	2.21	2.04	16.03
82	2.04	7.85	2.40	1.54	16.38
83	1.90	9.40	2.62	1.25	17.20
84	2.10	6.82	1.78	1.32	14.88
85	1.73	8.30	2.04	1.20	15.60
86	1.88	9.90	2.19	0.82	16.78
87	1.64	11.95	2.34	0.69	18.16
88	1.72	11.18	2.52	0.78	17.83
89	1.49	13.09	2.38	0.63	18.98
90	1.49	13.18	2.04	0.47	17.98
91	1.47	15.13	1.85	0.00	19.34
92	0.00	17.48	0.49	0.00	17.90

TABLE 3 (Continued)

Run No.	(15) Butyl- amine	(16) Dibutyl- amine	(17) N-Butylidene- butylamine	(18) Butyro- nitrile	(19) Total Base in L'
	Condensible Products--Moles				
62	0.0225	0.0570	0.0149	0.0195	0.0317
63	0.0215	0.0478	0.0147	0.0257	0.0360
64	0.0293	0.0327	0.0132	0.0372	0.0225
80	0.0326	0.0453	0.0158	0.0365	0.0244
81	0.0293	0.0505	0.0174	0.0296	0.0194
82	0.0279	0.0668	0.0189	0.0222	0.0160
83	0.0275	0.0728	0.0206	0.0181	0.0137
84	0.0280	0.0528	0.0139	0.0192	0.0187
85	0.0250	0.0642	0.0259	0.0173	0.0147
86	0.0258	0.0768	0.0172	0.0118	0.0115
87	0.0224	0.0927	0.0184	0.0100	0.0095
88	0.0236	0.0866	0.0192	0.0112	0.0089
89	0.0214	0.1013	0.0195	0.0091	0.0071
90	0.0204	0.1020	0.0161	0.0068	0.0060
91	0.0201	0.1172	0.0145	0.000	0.0042
92	0.000	0.1345	0.0038	0.000	0.0014

Run No.	(20) Moles of Gaseous Prods.	(21) Total Moles of Gaseous Prods.	(22) Butyl- amine in L'	(23) Ammonia in L'	(24) Total Butyl- amine	(25) Ammonia in Liquid Prods.
62	0.131	0.163	0.0067	0.0250	0.0292	0.001
63	0.158	0.204	0.0084	0.0276	0.0299	0.000
64	0.184	0.207	0.0085	0.0140	0.0378	0.011
80	0.182	0.206	0.0084	0.0160	0.0410	0.002
81	0.154	0.173	0.0071	0.0123	0.0364	0.005
82	0.114	0.130	0.0053	0.0107	0.0332	0.005
83	0.096	0.110	0.0045	0.0092	0.0320	0.006
84	0.098	0.117	0.0048	0.0139	0.0328	0.003
85	0.083	0.098	0.0040	0.0107	0.0290	0.003
86	0.066	0.077	0.0032	0.0083	0.0290	0.003
87	0.055	0.065	0.0026	0.0069	0.0250	0.005
88	0.066	0.075	0.0031	0.0058	0.0277	0.001
89	0.048	0.055	0.0023	0.0048	0.0237	0.001
90	0.040	0.046	0.0020	0.0040	0.0224	0.000
91	0.029	0.033	0.0014	0.0028	0.0215	0.003
92	0.014	0.016	0.0006	0.0008	0.0006	0.000

TABLE 3 (Continued

Run No.	(26) Total Ammonia Prod.	(27) 1-Butene in Liquid Prods.	(28) 1-Butene Prod.	(29) Hydrogen Prod.	(30) Conversion Fraction of Feed Butyl-amine	(31) Conversion Fraction of Feed Dibutyl-amine
62	0.026	0.0444	0.100	0.054	0.200	0.390
63	0.028	0.0540	0.112	0.066	0.205	0.327
64	0.025	0.0620	0.125	0.088	0.258	0.224
80	0.018	0.0613	0.112	0.089	0.262	0.290
81	0.017	0.0362	0.100	0.077	0.241	0.335
82	0.016	0.0446	0.087	0.063	0.220	0.403
83	0.015	0.0369	0.081	0.057	0.201	0.457
84	0.017	0.0504	0.087	0.052	0.241	0.388
85	0.014	0.0402	0.073	0.050	0.207	0.458
86	0.011	0.0346	0.063	0.041	0.198	0.525
87	0.012	0.0257	0.061	0.038	0.157	0.582
88	0.007	0.0285	0.054	0.042	0.184	0.577
89	0.006	0.0246	0.044	0.038	0.143	0.637
90	0.004	0.0146	0.035	0.030	0.149	0.682
91	0.006	0.0142	0.033	0.014	0.135	0.737
92	0.001	0.000	0.003	0.004	0.004	0.962

Run No.	(32) Conversion Fraction of Feed N-Butylidene-butylamine	(33) Conversion Fraction of Feed Butyro-nitrile	(34) Conversion Fraction of Feed 1-Butene	(35) Partial Pressure Butyl-amine	(36) Partial Pressure Dibutyl-amine
62	0.102	0.134	0.174	0.097	0.190
63	0.100	0.176	0.192	0.092	0.148
64	0.090	0.255	0.164	0.105	0.091
80	0.102	0.234	0.105	0.115	0.127
81	0.115	0.196	0.114	0.111	0.154
82	0.125	0.147	0.104	0.111	0.203
83	0.130	0.114	0.096	0.108	0.245
84	0.102	0.141	0.122	0.119	0.192
85	0.114	0.124	0.093	0.110	0.243
86	0.118	0.081	0.075	0.116	0.307
87	0.116	0.063	0.082	0.097	0.361
88	0.128	0.075	0.047	0.112	0.350
89	0.123	0.057	0.044	0.094	0.418
90	0.107	0.045	0.027	0.104	0.472
91	0.091	0.000	0.038	0.104	0.566
92	0.027	0.000	0.006	0.004	0.915

TABLE 3 (Continued)

Run No.	(37) N-Butylidene-butylamine	(38) Butyro-nitrile	(39) Ammonia	(40) 1-Butene	(41) Hydrogen
		Partial Pressure			
62	0.050	0.065	0.087	0.333	0.180
63	0.045	0.079	0.086	0.345	0.204
64	0.037	0.104	0.070	0.348	0.245
80	0.044	0.102	0.050	0.313	0.249
81	0.053	0.090	0.053	0.305	0.235
82	0.063	0.074	0.052	0.290	0.210
83	0.069	0.061	0.051	0.273	0.192
84	0.050	0.070	0.062	0.316	0.189
85	0.060	0.066	0.053	0.276	0.193
86	0.068	0.047	0.044	0.252	0.164
87	0.072	0.039	0.047	0.237	0.148
88	0.078	0.045	0.028	0.219	0.169
89	0.080	0.038	0.029	0.186	0.156
90	0.074	0.031	0.018	0.162	0.137
91	0.070	0.000	0.029	0.160	0.070
92	0.026	0.000	0.005	0.020	0.004

The results of the butylamine and dibutylamine runs are presented by Figures 3 through 17. Figures 3 through 9 present the results using catalyst A and Figures 10 through 17 present the results using catalyst B.

In Figure 3 is plotted the conversion, as moles of butylamine converted to each product per mole of butylamine in the feed, against the temperature of the salt bath for the catalyst activated at 500° in a vacuum. In Figures 10 and 11 are plotted the conversion, as moles of butylamine converted to each product per mole of butylamine in the

Figure 3.--Conversion of butylamine to products as a function of temperature over catalyst A-2 activated at 500° in a vacuum. 1/GSSV 11.2.

○ Dibutylamine
◐ N-Butylidenebutylamine
◑ Butyronitrile
◓ 1-Butene
◒ Unreacted butylamine
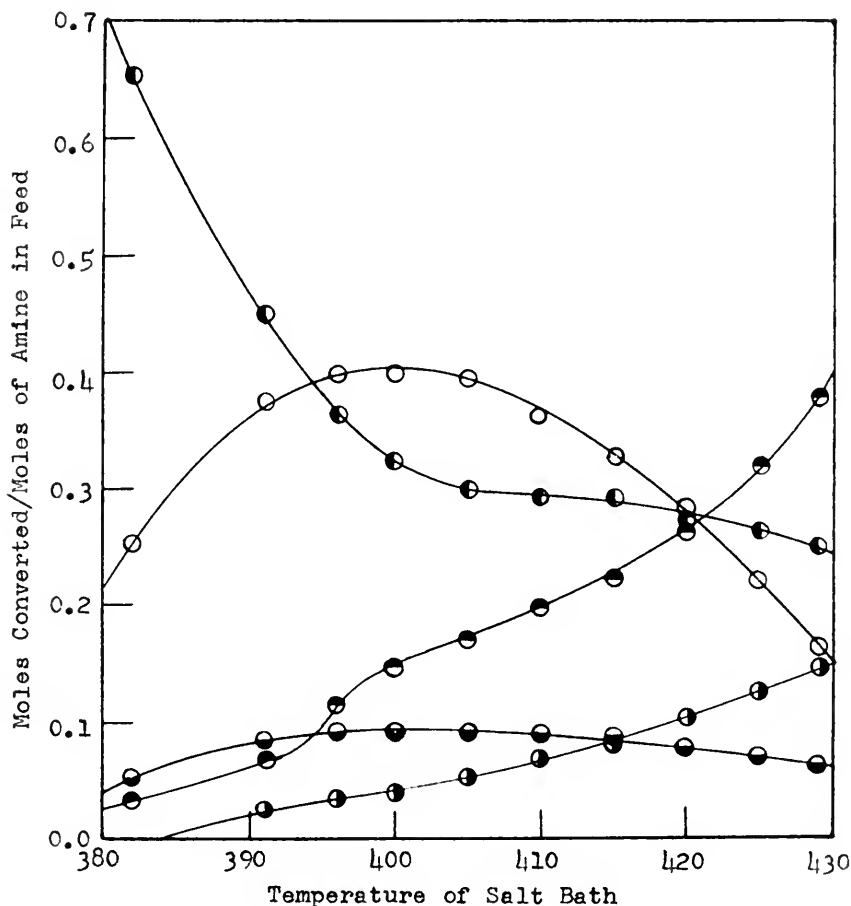
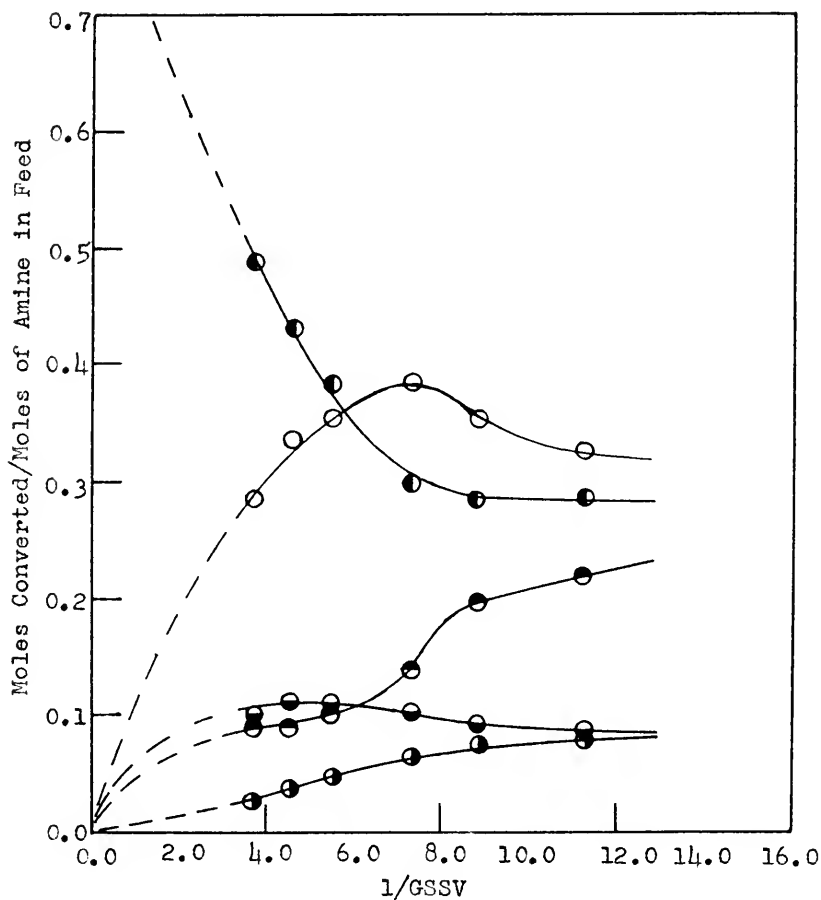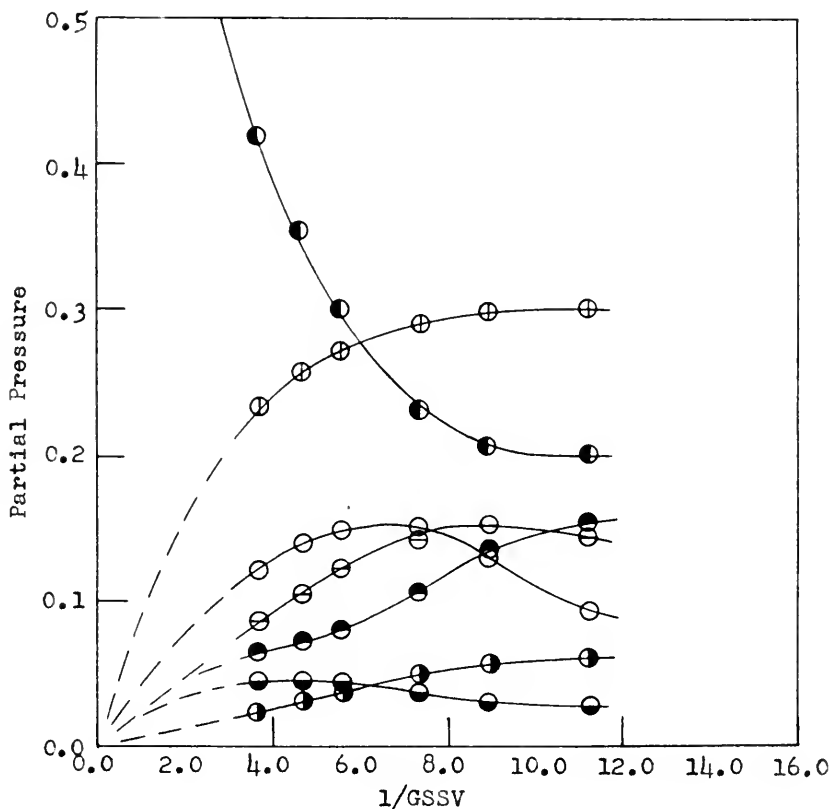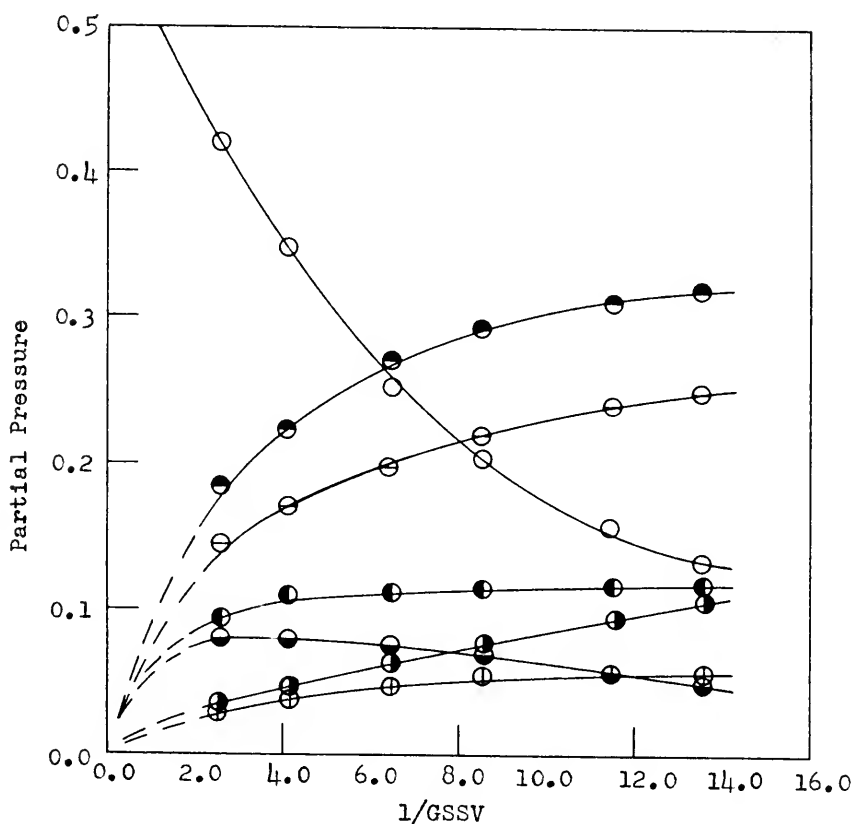Figure 4.--Conversion of butylamine to products as
a function of space velocity over catalyst A-2 activated at
500° in a vacuum. Temperature 415°.

○ Dibutylamine
◐ N-Butylidenebutylamine
◑ Butyronitrile
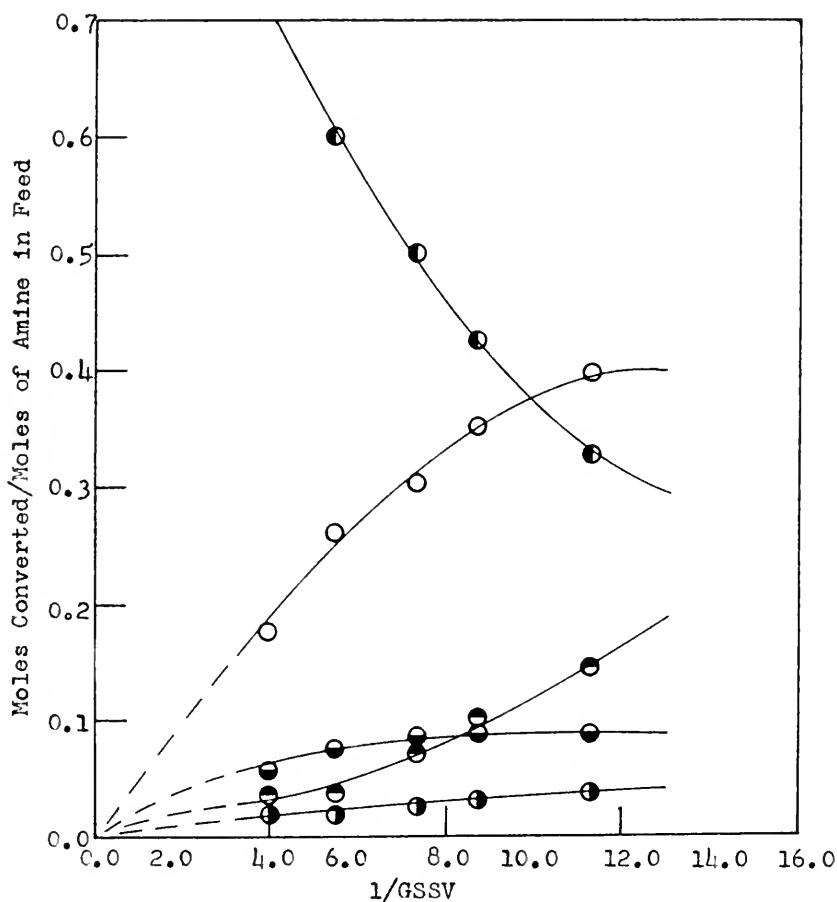◕ 1-Butene
◐ Unreacted butylamine

Figure 5.--Partial pressures of butylamine and products as a function of space velocity over catalyst A-2 activated at 500° in a vacuum. Temperature 415°.

    ○ Dibutylamine
    ◐ N-Butylidenebutylamine
    ◑ Butyronitrile
    ● 1-Butene
    ⊕ Ammonia
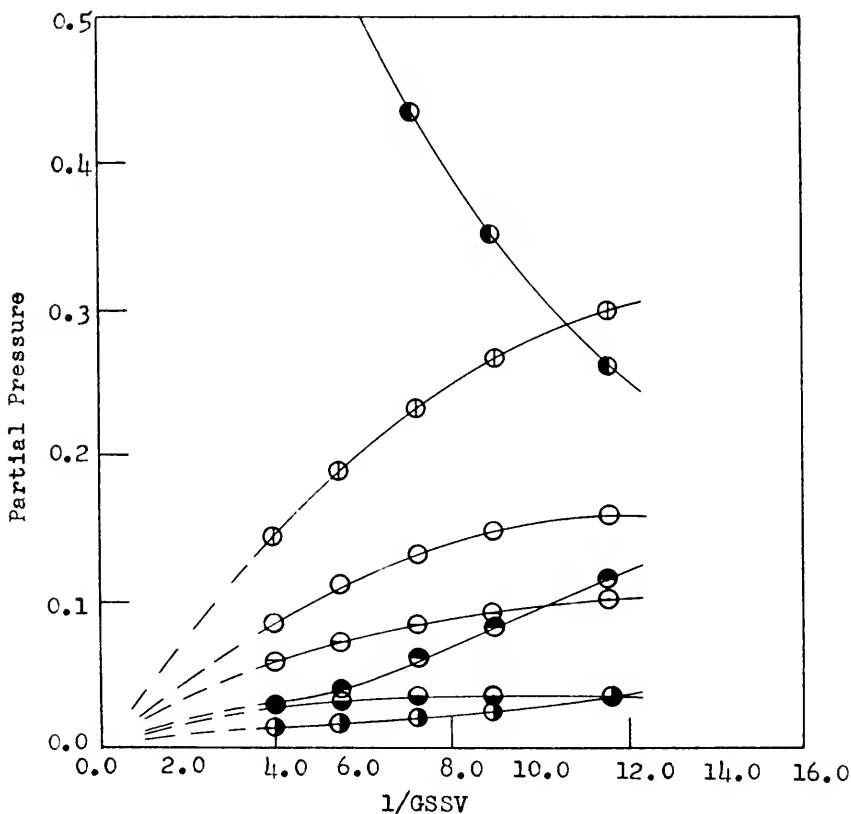   ⊖ Hydrogen
    ◑ Unreacted butylamine

Figure 6.--Partial pressures of dibutylamine and
products as a function of space velocity over catalyst
A-3 activated at 500° in a vacuum.   Temperature 425°.

◑ N-Butylidenebutylamine
◐ Butyronitrile
◑ Butylamine
◓ 1-Butene
① Ammonia
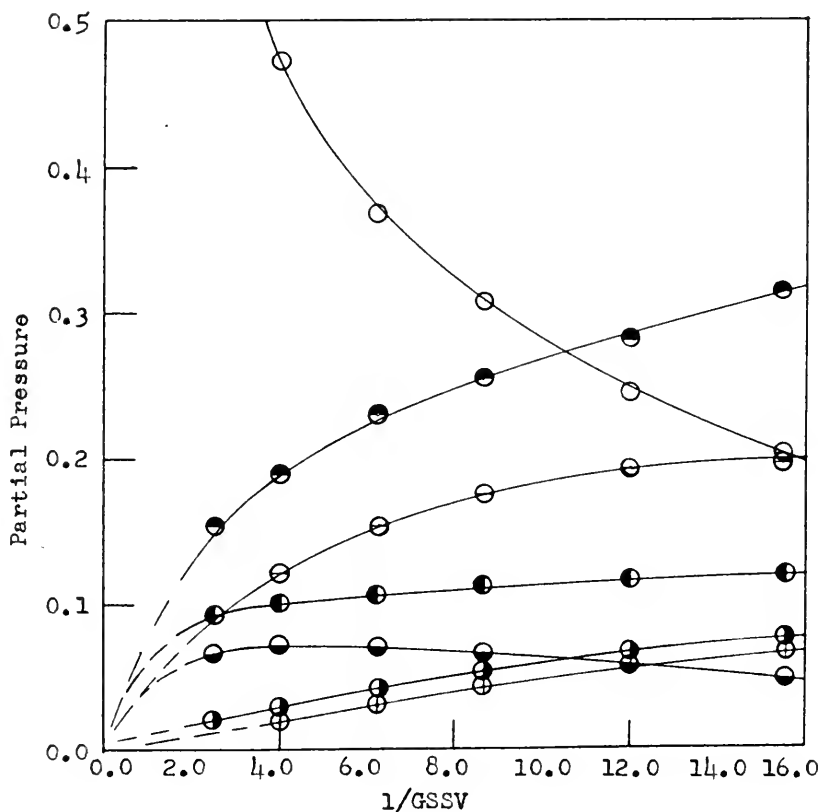⊖ Hydrogen
○ Unreacted dibutylamine

Figure 7.--Conversion of butylamine to products as
a function of space velocity over catalyst A-2 activated at
500° in a vacuum.   Temperature 400°.

        ○ Dibutylamine
        ◐ N-Butylidenebutylamine
        ◑ Butyronitrile
        ◒ 1-Butene
        ◐ Unreacted butylamine

Figure 8.--Partial pressures of butylamine and products as a function of space velocity over catalyst A-2 activated at 500° in a vacuum. Temperature 400°.

○ Dibutylamine
◑ N-Butylidenebutylamine
◐ Butyronitrile
◓ 1-Butene
◍ Ammonia
⊖ Hydrogen
◉ Unreacted butylamine

Figure 9.--Partial pressures of dibutylamine and products as a function of space velocity over catalyst A-3 activated at 500° in a vacuum. Temperature 410°.

◒ N-Butylidenebutylamine
◐ Butyronitrile
◑ Butylamine
● 1-Butene
◍ Ammonia
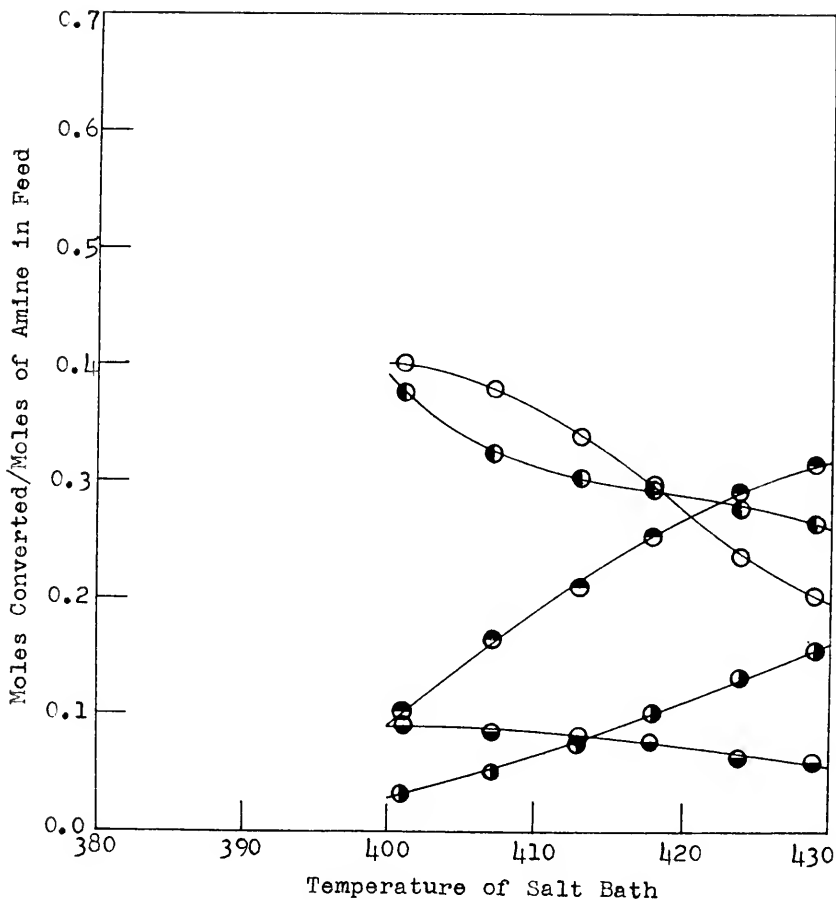⊖ Hydrogen
○ Unreacted dibutylamine

Figure 10.--Conversion of butylamine to products as a function of temperature over catalyst B-2 activated at 800° in a vacuum. 1/GSSV 10.0.

○ Dibutylamine
◑ N-Butylidenebutylamine
◐ Butyronitrile
◒ 1-Butene
◐ Unreacted butylamine

Figure 11.--Conversion of butylamine to products as a function of temperature over catalyst B-2 activated at 800° in a vacuum. 1/GSSV 12.1

○ Dibutylamine
◐ N-Butylidenebutylamine
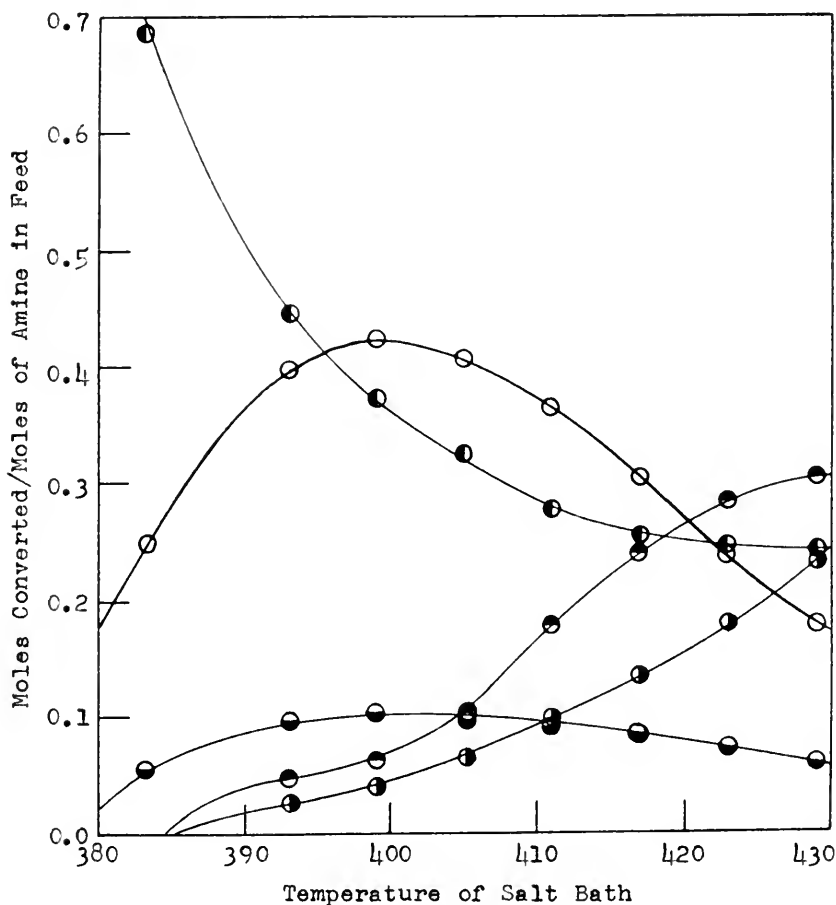◑ Butyronitrile
⊖ 1-Butene
⦿ Unreacted butylamine

Figure 12.--Conversion of butylamine to products as a function of space velocity over catalyst B-2 activated at 800° in a vacuum.   Temperature - 415°.

○ Dibutylamine
◑ N-Butylidenebutylamine
◐ Butyronitrile
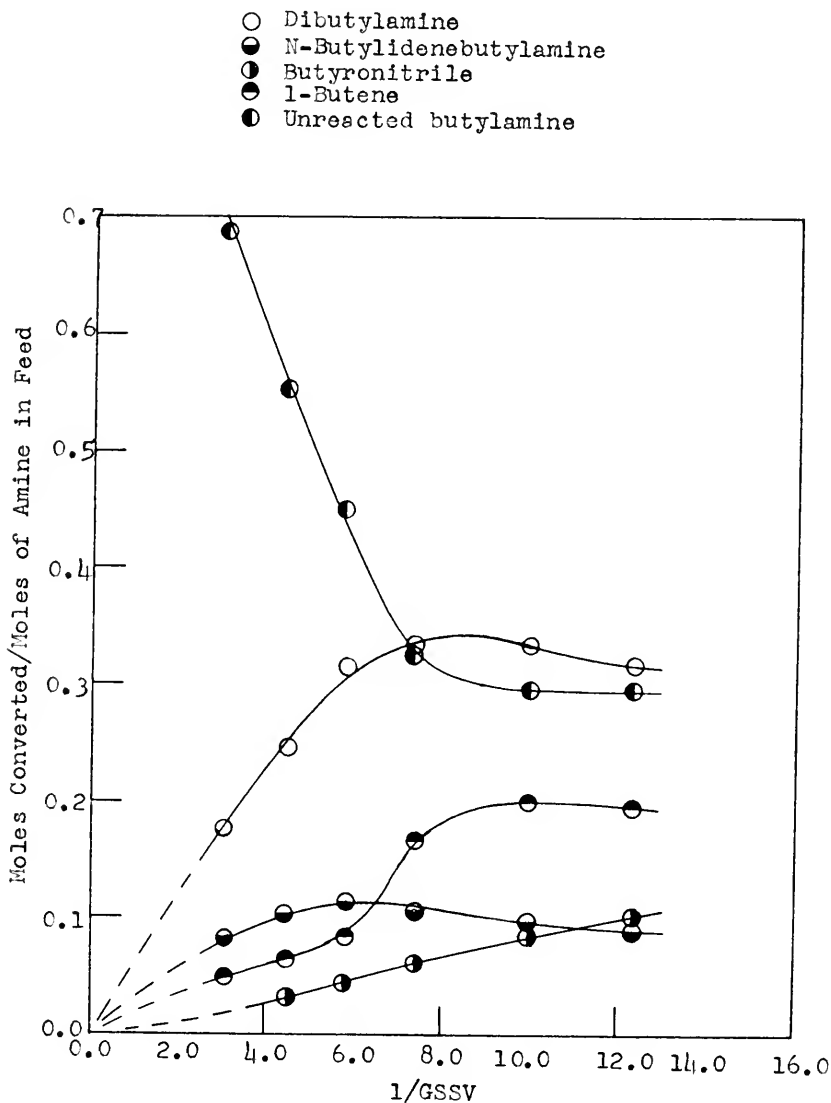● 1-Butene
◐ Unreacted butylamine

Figure 13.--Partial pressures of butylamine and products as a function of space velocity over catalyst B-2 activated at 800° in a vacuum. Temperature 415°.

○ Dibutylamine
◑ N-Butylidenebutylamine
◐ Butyronitrile
◐ 1-Butene
◒ Ammonia
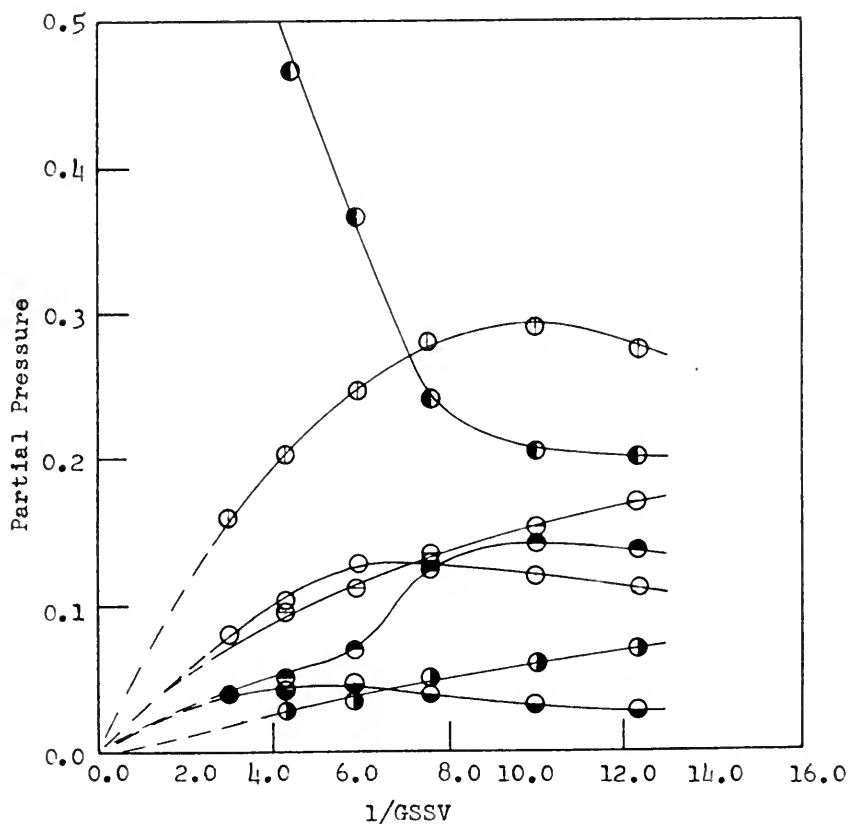⊖ Hydrogen
◑ Unreacted butylamine

Figure 14.--Conversion of butylamine to products as a function of space velocity over catalyst B-2 activated at 800° in a vacuum. Temperature 402°.

○ Dibutylamine
◕ N-butylidenebutylamine
◐ Butyronitrile
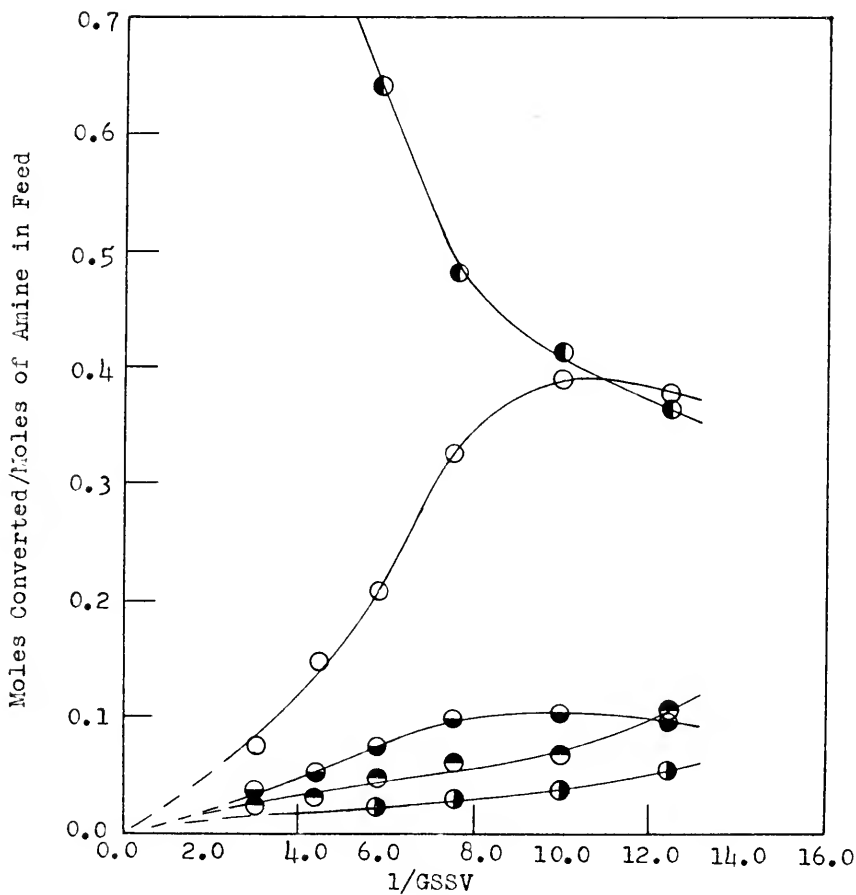⊖ 1-Butene
◑ Unreacted butylamine

Figure 15.--Partial pressures of butylamine and products as a function of space velocity over catalyst B-2 activated at 800° in a vacuum. Temperature 402°.

○   Dibutylamine
◓   N-Butylidenebutylamine
◐   Butyronitrile
◒   1-Butene
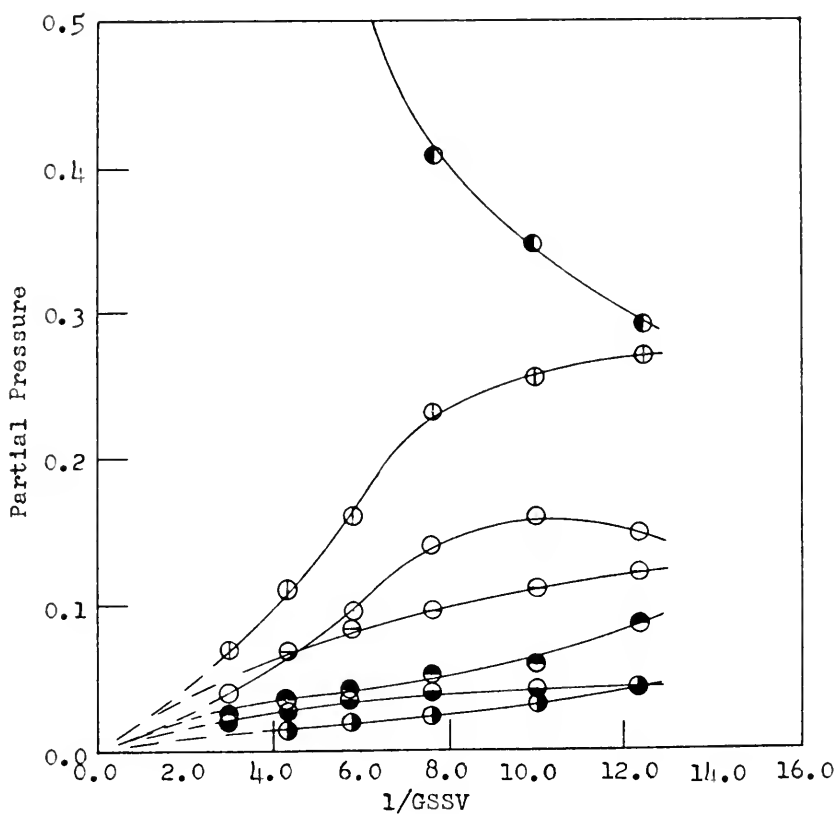◑   Ammonia
⊖   Hydrogen
◐   Unreacted butylamine

Figure 16.--Conversion of butylamine to products as a function of space velocity over catalyst B-3 activated at 800° in the Presence of water vapor. Temperature 415°.

○ Dibutylamine
◐ N-Butylidenebutylamine
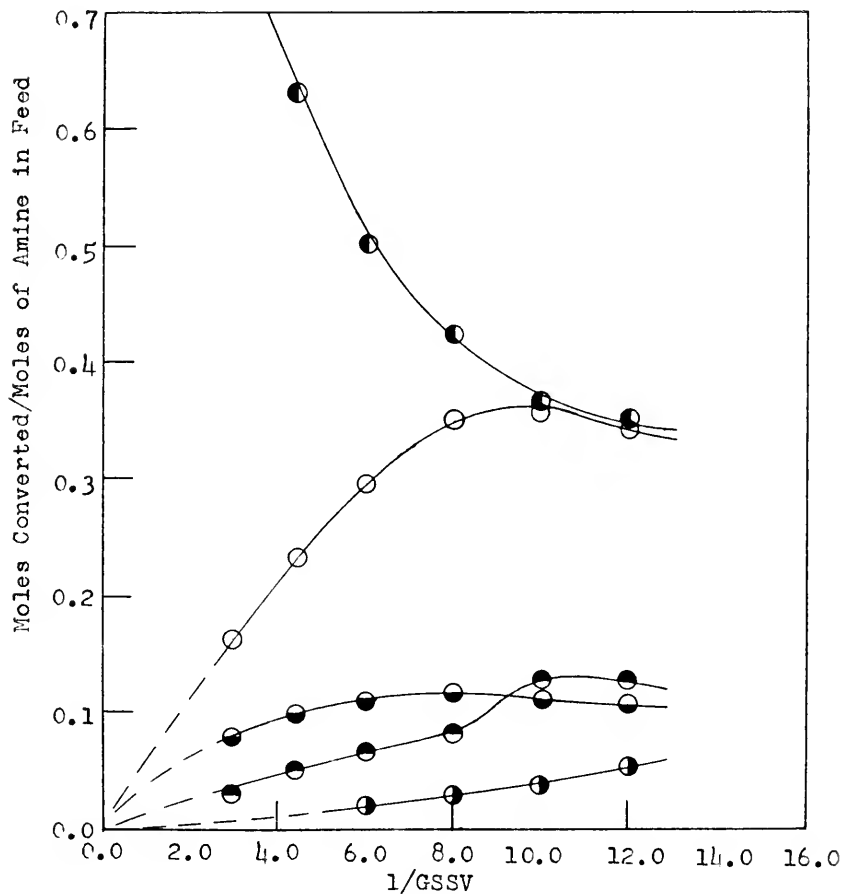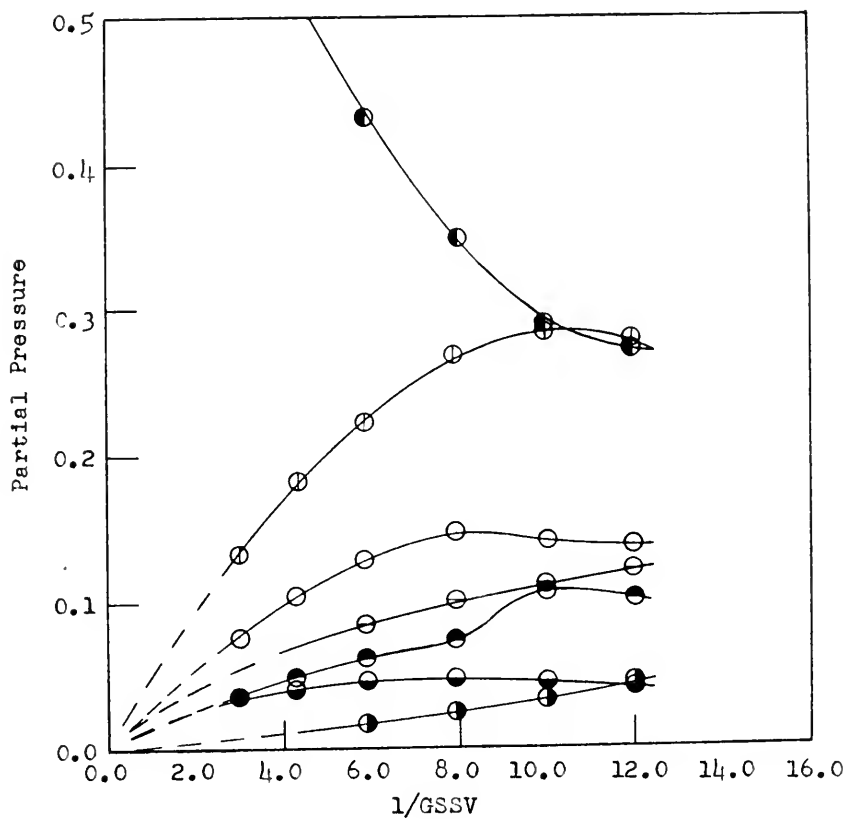◑ Butyronitrile
◓ 1-Butene
◑ Unreacted butylamine

Figure 17.--Partial pressures of butylamine and products as a function of space velocity over catalyst B-3 activated at 800° in the presence of water vapor. Temperature 415°.

     ○ Dibutylamine
     ◒ N-Butylidenebutylamine
     ◐ Butyronitrile
     ● 1-Butene
     ⦶ Ammonia
     ⊖ Hydrogen
     ◑ Unreacted butylamine

feed, against the temperature of the salt bath for the catalyst activated at 800° in a vacuum. Figure 10 represents the results obtained using the catalyst immediately after activation, while Figure 11 represents the results obtained using the same catalyst after it had been stored for several months.

In Figures 4 and 7 are plotted the conversion, as moles of butylamine converted to each product per mole of butylamine in the feed, against the reciprocal of the space velocity for the catalyst activated at 500° in a vacuum. In Figures 5 and 8 are plotted the partial pressures of the products formed by butylamine against the reciprocal of the space velocity for the catalyst activated at 500° in a vacuum. In Figures 6 and 9 are plotted the partial pressures of the products formed by dibutylamine against the reciprocal of the space velocity for the catalyst activated at 500° in a vacuum.

In Figures 12 and 14 are plotted the conversion, as moles of butylamine converted to each product per mole butylamine in the feed, against the reciprocal of the space velocity for the catalyst activated at 800° in a vacuum. In Figures 13 and 15 are plotted the partial pressures of the products formed by butylamine against the reciprocal of the space velocity for the catalyst activated at 800° in a vacuum. In Figure 16 is plotted the conversion, as

moles of butylamine converted to each product per mole of butylamine in the feed against the reciprocal of the space velocity for the catalyst activated at 800° in the presence of water vapor. In Figure 17 are plotted the partial pressures of the products formed by butylamine against the reciprocal of the space velocity for the catalyst activated at 800° in the presence of water vapor.

For the catalyst activated at 500° in a vacuum, the conversion to dibutylamine and N-butylidenebutylamine passes through a maximum, and the conversion to butyronitrile and 1-butene increases steadily as the temperature is increased. For the catalyst activated at 800° in a vacuum, the conversion to dibutylamine and N-butylidenebutylamine passes through a maximum, the conversion to butyronitrile increases steadily, and the conversion to 1-butene increases steadily and appeared to be approaching a maximum as the temperature was increased.

For the reaction temperatures above 400°, the conversion to dibutylamine and N-butylidenebutylamine passes through a maximum and the conversion to butyronitrile and 1-butene increases steadily as the contact time is increased. At 400° the feed rate was not reduced enough to permit the dibutylamine and N-butylidenebutylamine maxima to be reached but there seems no doubt that they could have been observed.

There was a consistent trend in activity with use during the first few runs or sets of runs. Runs 9, 10, and 15 were made separately and 11 and 12, and 13 and 14 were made in pairs over a sample of alumina, A-1, which had been activated at 500° in a vacuum. The results of these runs indicated that the activity of the catalyst was decreasing. Runs 17 through 21 were made over a fresh sample of alumina, A-2, from the same batch as used for the previous runs. Runs 17 and 21 were made under equivalent conditions and gave essentially the same results. The activity of this sample appeared to be the same as the activity of sample A-1 after it had decreased. Runs 22 through 37 were made over sample A-2. The results of runs 17 through 37 were used to plot Figures 3, 4, 5, 7, and 8. Runs 76 and 77 were made under equivalent conditions and with the same sample of alumina as used for runs 17 through 37 except that the catalyst was steamed for four hours at 430° between runs. The results of this pair of runs were essentially the same. Comparison of runs 76 and 77 with 17 and 21 indicated that the activity of the catalyst had increased slightly. Runs 78 and 79 were made under equivalent conditions using a fresh sample of alumina, A-4, which had been activated at 500° in a vacuum from a new batch except that the catalyst was steamed for five hours at 425° between runs. The results of this pair of runs

indicated that the activity of the catalyst had decreased slightly after being steamed.

Runs 38 through 42 were made over a sample of alumina, B-1, which had been activated at 800° in a vacuum and then stored for seven months. Runs 38 and 42 were made under equivalent conditions and gave essentially the same results. Run 61 was also made over sample B-1 after the catalyst had been stored for an additional two months. Comparison of run 61 with runs 38 through 42 indicates that the activity of the catalyst had increased. Runs 49 through 55 were made over a sample of alumina, B-2, immediately after it had been activated at 800° in a vacuum. Runs 65 through 73 were made over the same sample of alumina, B-2, after the catalyst had been stored for two months. Runs 65 and 69 were made under equivalent conditions and gave essentially the same results. Comparison of runs 65 through 69 with runs 49 through 55 indicates that the activity of the catalyst had increased. The results of runs 49 through 55 were used to plot Figure 10 and the results of runs 65 through 73 were used to plot Figure 11. Runs 65, 69, and 75 were made under equivalent conditions and with the same sample of alumina except that the catalyst was steamed for two hours at 400° prior to the 75th run. Comparison of the results of run 75 with the results of runs 65 and 69 indicates that the activity of the catalyst

had changed slightly but had neither increased nor decreased.
The per cent conversion to butyronitrile had decreased, the
per cent conversion to 1-butene had increased, and the per
cent conversion to dibutylamine and N-butylidenebutylamine
and the unreacted butylamine remained the same.

Runs 93 through 104 were made over sample B-2. The
results of runs 93 through 104 were used to plot Figures
12, 13, 14, and 15. Runs 105 through 110 were made over
a sample of alumina, B-3, immediately after it had been
activated at 800° in the presence of water vapor. The
results of runs 105 through 110 were used to plot Figures
16 and 17.

Runs 62 and 63, and 64 were made over a sample of
alumina, A-3, which had been activated at 500° in a vacuum;
these runs were made in order to obtain the products formed
by the reaction of dibutylamine over alumina. Runs 80
through 91 were also made over sample A-3. The results of
runs 80 through 91 were used to plot Figures 6 and 9.

Run 16 was made with butylamine in the absence of
a catalyst in order to determine if any reaction occurs by
thermal decomposition. The butylamine from this run was
recovered unreacted which indicates that no reaction occurs
by thermal decomposition. Run 92 was made with dibutylamine
in the absence of a catalyst in order to determine what
products, if any, are formed by the thermal decomposition

of dibutylamine. The dibutylamine from this run decomposed
into N-butylidenebutylamine, 1-butene, butylamine, and
ammonia. However, 96.2 per cent of the dibutylamine was
recovered unreacted which indicates that thermal decomposi-
tion accounts for only a small fraction of the reaction.

B. Discussion of Results

1. Path of Decomposition of Butylamine over Alumina

In order to evaluate the effects of changes in the
catalyst structure upon activity, the path of the reactions
which are taking place must be considered. The results of
this work on the decomposition of butylamine over alumina
have established the following points:

(1) Starting with butylamine, there are produced
ammonia, 1-butene, dibutylamine, N-butylidenebutylamine,
and butyronitrile in varying proportions, depending upon
the temperature, space velocity, and catalyst activity.

(2) Starting with dibutylamine, there are produced
1-butene, butylamine, ammonia, N-butylidenebutylamine, and
butyronitrile, the relative amounts in this case also
depend on the conditions.

(3) Starting with butylamine at sufficiently high
temperatures, the dibutylamine and N-butylidenebutylamine
contents of the products pass through a maximum and then
fall off. As the dibutylamine and N-butylidenebutylamine

contents of the products fall off, the butyronitrile content of the products increases.

(4) Starting with dibutylamine, the 1-butene, N-butylidenebutylamine, and butyronitrile contents of the products are larger than when starting with butylamine.

The various possible reactions which may be involved in the overall process are:

(a) $C_4H_9-NH_2 \rightleftharpoons C_3H_7-CH=NH + H_2$
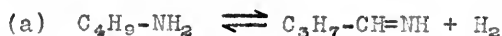
Although no butyl imine was found in the reaction products, the possibility of this reaction taking place could not be ruled out. If this material did form, it must have been lost by subsequent rapid reaction.
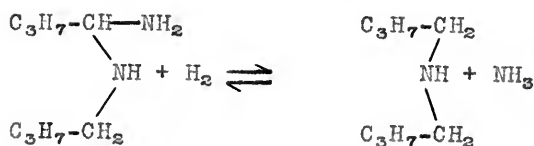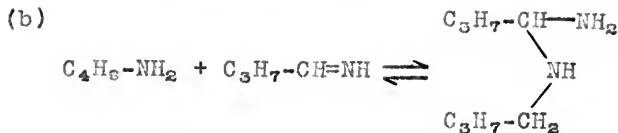
(b)

$$C_4H_9-NH_2 + C_3H_7-CH=NH \rightleftharpoons \begin{matrix} C_3H_7-CH-NH_2 \\ | \\ NH \\ | \\ C_3H_7-CH_2 \end{matrix}$$

$$\begin{matrix} C_3H_7-CH-NH_2 \\ | \\ NH \\ | \\ C_3H_7-CH_2 \end{matrix} + H_2 \rightleftharpoons \begin{matrix} C_3H_7-CH_2 \\ | \\ NH \\ | \\ C_3H_7-CH_2 \end{matrix} + NH_3$$

Dibutylamine is produced quite rapidly in the initial stages of the reaction, indicating that it comes directly from the butylamine. However, because of the rapid initial production of dibutylamine and the small partial pressure of hydrogen at small reaction times, conversion to the dibutylamine by this particular pathway seems to be a

relatively unimportant reaction.

(c) $C_3H_7-CH=NH \rightleftharpoons C_3H_7-C\equiv N + H_2$
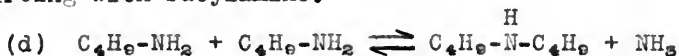
This reaction cannot be a major source of butyronitrile because of the fact that the butyronitrile content of the products is larger when starting with dibutylamine than when starting with butylamine.

(d) $C_4H_9-NH_2 + C_4H_9-NH_2 \rightleftharpoons C_4H_9-\overset{H}{N}-C_4H_9 + NH_3$

Dibutylamine is produced quite rapidly in the initial stages of the reaction, indicating that it comes directly from the butylamine as mentioned above. It is not possible from the results to exclude all contribution from process (b), but the present reaction seems to be the predominating reaction.

(e) $C_4H_9-NH_2 \rightleftharpoons C_2H_5-CH=CH_2 + NH_3$
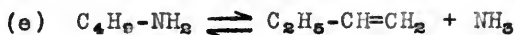
The occurrence of the forward reaction is indicated by the fact that some 1-butene production occurs at small times of reaction.

(f) $C_4H_9-\overset{H}{N}-C_4H_9 \rightleftharpoons C_4H_9-NH_2 + C_2H_5-CH=CH_2$

Starting with dibutylamine, 1-butene and butylamine are produced quite rapidly in the initial stages of the reaction, indicating that they come directly from the dibutylamine. Also, starting with butylamine, the rate of formation of 1-butene rises rapidly as the dibutylamine concentration approaches a maximum, indicating that 1-butene is produced by a reaction other than (e).

$$(g) \quad \overset{H}{C_4H_9\text{-}N\text{-}C_4H_9} \rightleftharpoons C_3H_9\text{-}CH=N\text{-}C_4H_9 + H_2$$

Starting with butylamine, N-butylidenebutylamine concentration reaches a maximum as the dibutylamine concentration reaches a maximum, and then falls off.

$$(h) \quad C_3H_7\text{-}CH=N\text{-}C_4H_9 \rightleftharpoons C_3H_7\text{-}C\equiv N + C_2H_5\text{-}CH=CH + H_2$$
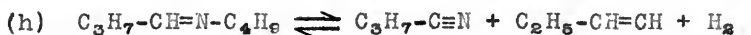
Butyronitrile production is small at small times of reaction and increases steadily as the N-butylidenebutylamine concentration passes through a maximum and falls off.
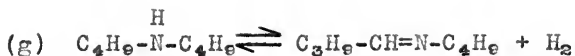
The ratios of partial pressures for reactions (d), (e), (f), (g), and (h) were calculated from the results of the butylamine runs at 415° and 400° for all forms of the catalyst. The ratios for reactions (d), (e), and (g) showed no agreement for any set of runs using the same catalyst, and, as a result, the ratios were of no value for determining the equilibria involved in these reactions. The ratios for reaction (h) increased as the reaction times were increased for all sets of runs using the same catalyst which indicates that the equilibrium for this reaction was not attained. The ratios for reaction (f) showed some agreement for any set of runs using the same catalyst and the averages for any set of runs at one temperature showed fair agreement for all forms of the catalyst. The values for the ratios calculated from the butylamine runs at 415° over catalysts A-2, B-2, and B-3; and from the butylamine runs at 400° over catalysts A-2 and B-2 are given in Table 4. The

ratios are tabulated in increasing order of reaction times.

TABLE 4

RATIOS OF PARTIAL PRESSURES FOR REACTION (f)

415 A-2	415 B-2	415 B-3	400 A-2	400 B-2
0.258	0.364	0.200	0.261	0.456
0.173	0.225	0.238	0.126	0.116
0.175	0.183	0.205	0.201	0.252
0.163	0.244	0.161	0.212	0.166
0.214	0.253	0.218	0.189	0.103
0.358	0.246	0.208		0.167
0.223[a]	0.256[a]	0.205[a]	0.198[a]	0.210[a]

[a] Average Values

The initial reactions in the butylamine decomposition appear to be (d) and (e). The dibutylamine produced by (d) appears to react according to either (f) or (g). The final reaction appears to be the decomposition of the N-butylidene-butylamine, produced by (g), by (h). The end products are 1-butene and butyronitrile, along with hydrogen and ammonia.

2. Activity and Changes in the Alumina Surface

The surface area of the catalysts used for this study was not determined. The variations in surface area

of alumina with increasing temperatures of activation have
been studied by other workers and the results show that for
temperatures of activation above 600° the surface area de-
creases. Because of this fact, the total activity of the
catalysts activated at 800° should be smaller than the total
activity of the catalysts activated at 500° provided the
specific activity of the catalysts is the same. Before
comparing total activity and specific activity of the
catalysts with activation temperatures, the relationship
between catalyst activity and the temperature of activation
of the catalyst will be considered.

Inspection of Figures 4 and 12, 5 and 13, and 7 and
14 indicates the relationship between the dehydrogenation
activity of the catalysts and the temperature of activation
of the catalysts in a qualitative way. These figures, in
view of the fact that temperatures of activation above 600°
result in a decrease in surface area, show that the catalyst
activated at 800° in a vacuum is more active for dehydro-
genation reactions than the catalyst activated at 500° in
a vacuum as indicated by the per cent conversion of butyl-
amine to butyronitrile and the partial pressures of butyro-
nitrile and hydrogen in the reaction products. The more
active dehydrogenation catalyst would be expected to in-
crease the rates of reactions (g) and (h), and, as a result,
the per cent conversion of butylamine to dibutylamine would

be smaller than the per cent conversion of butylamine to
dibutylamine for the less active dehydrogenation catalyst.
Inspection of Figures 4 and 12 reveals this fact. The more
active dehydrogenation catalyst would also be expected to
shift reaction (f) to the left in order to maintain equi-
librium, because of the increased conversion of the di-
butylamine to N-butylidenebutylamine, and, as a result,
the per cent conversion of butylamine to 1-butene would
be smaller than the per cent conversion of butylamine to
1-butene for the less active dehydrogenation catalyst.
Inspection of Figures 4 and 12 confirms this supposition
also.

Inspection of Figures 3 and 11, in which are
plotted the moles of butylamine converted to each product
per moles of amine in feed against the temperature, also
indicates that the catalyst activated at 800° in a vacuum
is more active for dehydrogenation reactions than the
catalyst activated at 500° in a vacuum as indicated by
the larger per cent conversion of butylamine to butyro-
nitrile.

The relationship between the total activity of the
catalyst and the temperature of activation of the catalyst
can be obtained by comparing Figures 4 and 12, and 7 and 14.
Inspection of these figures shows that the total activity
of the catalyst decreases with increasing temperatures of

activation as expected from the decrease in surface area with increasing temperatures of activation.

The relationship between specific activity and the temperature of activation of the catalyst can be obtained by comparing Figures 4 and 12, 5 and 13, 7 and 14, and 8 and 15, and the results obtained by Brey and Krieger on the surface area of alumina as a function of temperature. Brey and Krieger found that the surface area of alumina is constant after heat treatment up to 500° and decreases about 42 per cent after heat treatment at 800°. The total activity of the catalyst activated at 800° is slightly smaller than the total activity of the catalyst activated at 500° but the decrease in total activity does not appear to be nearly as great as would be expected from the difference in surface areas. This indicates that the specific activity of the catalyst activated at 800° is larger than the specific activity of the catalyst activated at 500°. This increase in specific activity can be accounted for by examination of the effects of the more active dehydrogenation catalyst. The shifting of reaction (f) to the left, as mentioned above, results in a larger conversion of butylamine to products and, as a result, the specific activity of the catalyst activated at 800° should be greater than the specific activity of the catalyst activated at 500°.

The increased dehydrogenation activity of the catalyst activated at 800° may be caused by the partial conversion of the surface of the catalyst to another form. The X-ray diffraction patterns of the alumina samples activated at 500° and 800° showed that both samples contained gamma alumina and that the degree of crystallinity of both samples was about the same. In spite of these results, there is a possibility that the surface of the alumina activated at 800° has been partially converted to the alpha form. Boreskov, Dzis'ko, Borisova, and Krasnopol'skaya found that alpha alumina was mainly a dehydrogenation catalyst, and, in view of this fact, the increased dehydrogenation activity of the catalyst activated at 800° may be caused by the partial conversion of the surface of the alumina to the alpha form.

The relationship between the total activity of the catalysts activated at 800° in a vacuum and in the presence of water vapor can be obtained by comparing Figures 12 and 16. Inspection of these figures indicates that the total activity of the catalyst activated in the presence of water vapor has decreased. The results obtained by Brey and Krieger on the surface area of alumina activated at 800° in a vacuum and in the presence of water vapor show that there is about a 50 per cent decrease in surface area after activation in the presence of water vapor. The decrease in

total activity, in view of this fact, appears to be caused by a decrease in surface area. The specific activity of the catalysts activated at 800° in a vacuum and in the presence of water vapor, in view of the smaller surface area of the catalyst activated at 800° in the presence of water vapor, appear to be about the same.

The change in activity of the catalyst with use was observed but was not studied. It was found that by evacuating the reaction tube after each run and filling the latter with argon that the activity of the catalyst did not change with use. The increase in activity with use observed for the catalyst activated at 800° was probably a result of steaming the catalyst between the set of runs represented by Figure 10 and the set of runs represented by Figure 11.

SECTION V

SUMMARY

(1)   The products of the decomposition of n-butyl
amine over alumina at elevated temperatures have been
separated and identified.   The products are ammonia, 1-
butene, hydrogen, dibutylamine, N-butylidenebutylamine,
and butyronitrile together with traces of ethylene and
methane.

(2)   The catalytic activity of samples of alumina
prepared by heating at 500° and 800° in a vacuum has been
measured for the decomposition of butylamine as a function
of temperature between 380° and 430°.

(3)   The catalytic activity of samples of alumina
prepared by heating at 500° and 800° in a vacuum and at
800° in the presence of water vapor has been measured for
the decomposition of butylamine as a function of the re-
ciprocal of the space velocity at 415° and 400°.

(4)   The catalytic activity of a sample of alumina
prepared by heating at 500° in a vacuum has been measured
for the decomposition of dibutylamine as a function of the
reciprocal of the space velocity at 415° and 400°.

84

(5)   The probable path of the decomposition of butylamine over alumina at elevated temperatures has been established in the light of the results obtained from the decomposition of butylamine and dibutylamine as a function of the reciprocal of the space velocity.

(6)   The catalyst activated at 800° in a vacuum, in view of the decrease in surface area with activation temperatures above 600°, has been shown to be a more active catalyst for dehydrogenation reactions than the catalyst activated at 500°, in a vacuum.

(7)   It has been shown that the total activity of the catalyst activated at 800° in a vacuum is smaller than the total activity of the catalyst activated at 500° in a vacuum, and that the total activity of the catalyst activated at 800° in the presence of water vapor is smaller than the total activity of the catalyst activated at 800° in a vacuum.

APPENDIX

PART I

Per Cent Weight Determinations

The results of the procedure used to analyze the
condensible products are tabulated in per cent weight since
known weights of the compounds were used to prepare the
mixtures. The fractions of the total volume were first
determined and, from these and the total volume, the milli-
liters of the compounds were calculated. The weights of
the compounds were calculated from the milliliters and the
densities of the compounds. The per cent weights were cal-
culated from the weights of the separate compounds and the
total weight of the mixture.

	Butyl-amine		Dibutyl-amine		n-Butylidene-n-butylamine		Butyro-nitrile	
	Act.	Cal.	Act.	Cal.	Act.	Cal.	Act.	Cal.
(1)	45.1	45.5	51.7	51.8	3.2	2.6		
(2)	74.5	75.1	19.2	19.6	6.3	5.1		
(3)	53.3	53.0	37.6	38.6	9.1	8.4		
(4)	59.9	59.4	27.1	28.3	12.8	12.2		
(5)	41.9	42.4	48.1	47.4	3.0	2.6	7.0	7.6
(6)	58.1	58.8	15.0	14.7	4.9	4.5	22.1	22.0
(7)	46.6	46.4	32.8	32.8	7.9	7.8	12.7	12.7
(8)	49.9	49.6	22.5	22.8	10.7	10.8	16.9	16.9

PART II

Material Balances

The results of the material balances obtained
for the eight runs are tabulated in moles. Line (18)
gives the difference between the calculated moles of
1-butene produced and the actual moles of 1-butene
found by analysis--line (11) plus line (14). The re-
sults are low as expected due to the formation of
ethylene and methane. Line (19) gives the difference
between the moles of hydrogen found by analysis and
the calculated moles of hydrogen produced. The results
are low as expected due to decomposition which is evident
by the presence of ethylene and methane. Line (20) gives
the difference between the moles of hydrogen which would
be formed by the decomposition of (18) and the moles
accounted for by ethylene and methane which should give
the same result as (19). The eighth run was made in the
absence of a catalyst in order to determine if any re-
action occurs by thermal decomposition.

Run No. 9 - 0.226 moles of butylamine passed over
catalyst at 425° at a reciprocal space velocity of 11.2.

(1) Butylamine collected in receiver I. 0.0418

(2) Dibutylamine. 0.0246

(3) N-Butylidenebutylamine. 0.0074

(4) Butyronitrile 0.0437

(5) Base collected in receiver L' 0.0980

(6) Butylamine collected in receiver L' 0.0104

(7) Ammonia collected in receiver L'. 0.0876

(8) Total Butylamine Unreacted. 0.0522

(9) Ammonia dissolved in condensible products . . . 0.010

(10) Total ammonia produced. 0.098

(11) 1-Butene dissolved in condensible products. . . 0.0239

(12) 1-Butene produced 0.066

(13) Hydrogen produced 0.095

(14) 1-Butene in gaseous products. 0.0319

(15) Ethylene in gaseous products. 0.0016

(16) Hydrogen in gaseous products. 0.1142

(17) Methane in gaseous products 0.0087

(18) 1-Butene difference 0.010

(19) Hydrogen difference 0.019

(20) Hydrogen produced by decomposition. 0.019

Run No. 10 - 0.226 moles of butylamine passed over catalyst at 418° at a reciprocal space velocity of 11.2.

(1) Butylamine collected in receiver I. 0.0467

(2) Dibutylamine. 0.0324

(3) N-Butylidenebutylamine. 0.0089

(4) Butyronitrile 0.0351

(5) Base collected in receiver L' 0.0936

(6) Butylamine collected in receiver L' 0.0089

(7) Ammonia collected in receiver L'. 0.0847

(8) Total Butylamine Unreacted. 0.0552

(9) Ammonia dissolved in condensible products . . . 0.009

(10) Total ammonia produced. 0.094

(11) 1-Butene dissolved in condensible products. . . 0.0214

(12) 1-Butene produced 0.053

(13) Hydrogen produced 0.079

(14) 1-Butene in gaseous products. 0.0244

(15) Ethylene in gaseous products. 0.0015

(16) Hydrogen in gaseous products. 0.0922

(17) Methane in gaseous products 0.0078

(18) 1-Butene difference 0.007

(19) Hydrogen difference 0.013

(20) Hydrogen produced by decomposition. 0.009

Run No. 11 - 0.226 moles of butylamine passed over catalyst at 417° at a reciprocal space velocity of 11.2.

(1) Butylamine collected in receiver I. 0.0593

(2) Dibutylamine. 0.0371

(3) N-Butylidenebutylamine. 0.0103

(4) Butyronitrile 0.0187

(5) Base collected in receiver L' 0.0989

(6) Butylamine collected in receiver L' 0.0077

(7) Ammonia collected in receiver L'. 0.0913

(8) Total butylamine unreacted. 0.0670

(9) Ammonia dissolved in condensible products . . . 0.002

(10) Total ammonia produced. 0.093

(11) 1-Butene dissolved in condensible products. . . 0.0112

(12) 1-Butene produced 0.046

(13) Hydrogen produced 0.048

(14) 1-Butene in gaseous products. 0.0315

(15) Ethylene in gaseous products. 0.000

(16) Hydrogen in gaseous products. 0.0499

(17) Methane in gaseous products 0.0048

(18) 1-Butene difference 0.003

(19) Hydrogen difference 0.002

(20) Hydrogen produced by decomposition. 0.002

Run No. 12 - 0.226 moles of butylamine passed over catalyst at 430° at a reciprocal space velocity of 11.2.

(1) Butylamine collected in receiver I. 0.0485

(2) Dibutylamine. 0.0205

(3) N-Butylidenebutylamine. 0.0076

(4) Butyronitrile 0.0351

(5) Base collected in receiver L' 0.1124

(6) Butylamine collected in receiver L' 0.0109

(7) Ammonia collected in receiver L'. 0.1015

(8) Total butylamine unreacted. 0.0594

(9) Ammonia dissolved in condensible products . . . 0.002

(10) Total ammonia produced. 0.104

(11) 1-Butene dissolved in condensible products. . . 0.0157

(12) 1-Butene produced 0.075

(13) Hydrogen produced 0.078

(14) 1-Butene in gaseous products. 0.0475

(15) Ethylene in gaseous products. 0.0015

(16) Hydrogen in gaseous products. 0.0923

(17) Methane in gaseous products 0.0078

(18) 1-Butene difference 0.013

(19) Hydrogen difference 0.014

(20) Hydrogen produced by decomposition. 0.023

Run No. 13 - 0.226 moles of butylamine passed over catalyst at 422° at a reciprocal space velocity of 11.2.

(1) Butylamine collected in receiver I. 0.0575

(2) Dibutylamine. 0.0290

(3) N-Butylidenebutylamine. 0.0095

(4) Butyronitrile 0.0244

(5) Base collected in receiver L' 0.1042

(6) Butylamine collected in receiver L' 0.0090

(7) Ammonia collected in receiver L'. 0.0952

(8) Total butylamine unreacted. 0.0665

(9) Ammonia dissolved in condensible products . . . 0.003

(10) Total ammonia produced. 0.098

(11) 1-Butene dissolved in condensible products. . . 0.0082

(12) 1-Butene produced 0.058

(13) Hydrogen produced 0.058

(14) 1-Butene in gaseous products. 0.0456

(15) Ethylene in gaseous products. 0.000

(16) Hydrogen in gaseous products. 0.0647

(17) Methane in gaseous products 0.0049

(18) 1-Butene difference 0.004

(19) Hydrogen difference 0.007

(20) Hydrogen produced by decomposition. 0.006

Run No. 14 - 0.226 moles of butylamine passed over
catalyst at 422° at a reciprocal space velocity of 9.3.

(1) Butylamine collected in receiver I. 0.0572

(2) Dibutylamine. 0.0340

(3) N-Butylidenebutylamine. 0.0106

(4) Butyronitrile 0.0206

(5) Base collected in receiver L' 0.1008

(6) Butylamine collected in receiver L' 0.0081

(7) Ammonia collected in receiver L'. 0.0927

(8) Total butylamine unreacted. 0.0653

(9) Ammonia dissolved in condensible products . . 0.003

(10) Total ammonia produced. 0.096

(11) 1-Butene dissolved in condensible products. . 0.0073

(12) 1-Butene produced 0.051

(13) Hydrogen produced 0.052

(14) 1-Butene in gaseous products. 0.0352

(15) Ethylene in gaseous products. 0.0007

(16) Hydrogen in gaseous products. 0.0557

(17) Methane in gaseous products 0.0068

(18) 1-Butene difference 0.008

(19) Hydrogen difference 0.004

(20) Hydrogen produced by decomposition. 0.018

Run No. 15 - 0.226 moles of butylamine passed over catalyst at 418° at a reciprocal space velocity of 11.2

(1) Butylamine collected in receiver I. 0.0542

(2) Dibutylamine. 0.0325

(3) N-Butylidenebutylamine. 0.0093

(4) Butyronitrile 0.0228

(5) Base collected in receiver L' 0.0996

(6) Butylamine collected in receiver L' 0.0082

(7) Ammonia collected in receiver L'. 0.0914

(8) Total butylamine unreacted. 0.0624

(9) Ammonia dissolved in condensible products . . . 0.008

(10) Total ammonia produced. 0.099

(11) 1-Butene dissolved in condensible products. . . 0.0084

(12) 1-Butene produced 0.057

(13) Hydrogen produced 0.055

(14) 1-Butene in gaseous products. 0.0299

(15) Ethylene in gaseous products. 0.0013

(16) Hydrogen in gaseous products. 0.0552

(17) Methane in gaseous products 0.0163

(18) 1-Butene difference 0.019

(19) Hydrogen difference 0.000

(20) Hydrogen produced by decomposition. 0.030

Run No. 16 - 0.151 moles of butylamine passed
through reaction tube at 430° at a reciprocal space
velocity of 11.2.

(1) Butylamine collected in receiver I. 0.151

(2) Dibutylamine. C.000

(3) N-Butylidenebutylamine. 0.000

(4) Butyronitrile 0.000

(5) Base collected in receiver L' 0.000

(6) Butylamine collected in receiver L' 0.000

(7) Ammonia collected in receiver L'. C.000

(8) Total butylamine unreacted. 0.000

(9) Ammonia dissolved in condensible products . . . 0.000

(10) Total ammonia produced. C.0C0

(11) 1-Butene dissolved in condensible products. . . 0.000

(12) 1-Butene produced C.000

(13) Hydrogen produced 0.000

(14) 1-Butene in gaseous products. C.000

(15) Ethylene in gaseous products. C.000

(16) Hydrogen in gaseous products. C.000

(17) Methane in gaseous products C.0C0

(18) 1-Butene difference C.000

(19) Hydrogen difference C.000

(20) Hydrogen produced by decomposition. 0.000

BIBLIOGRAPHY

(1) Boreskov, Dzis'ko, and Borisova, Zhur. Fiz. Khim.,
     27, 1176-80 (1953); C. A. 48: 5628.

(2) Boreskov, Dzis'ko, Borisova, and Krasnopol'skaya,
     Zhur. Fiz. Khim., 26, 492-9 (1950); C. A. 47: 957.

(3) Breiner and Gandillon, Helv. Chem. Acta, 14, 1283-
     307 (1931); C. A. 26: 1575.

(4) Brey and Krieger, J. Am. Chem. Soc., 71, 3637-41
     (1949).

(5) Brooks, Murdock, and Zahn, Anal. Chem., 20, 62-3.

(6) Brown and Reid, J. Phys. Chem., 28, 1067-76 (1924).

(7) Campbell, Sommers, and Campbell, J. Am. Chem. Soc.,
     66, 82 (1944).

(8) Clarke, O'Leary, and Karabinos, J. Am. Chem. Soc.,
     74, 5587-8 (1952).

(9) Dorrell, J. Chem. Soc., 127, 2399-407 (1925).

(10) Egly and Smith, Chem. Engrs. Progress, 44, No. 5,
     Trans. Am. Inst. Chem. Engrs., 387-98 (1948).

(11) Emerson, Hess, and Uhle, J. Am. Chem. Soc., 63,
     872 (1941).

(12) Jeffery and Vogel, J. Chem. Soc., 674 (1948).

(13) Kreiger, J. Am. Chem. Soc., 63, 2712-14 (1941).

(14) Matuszak, Ind. and Eng. Chem. Anal. Ed., 10, 354.

(15) N. V. de Bataafsche Maatschappij, Dutch 65, 644,
     May 15, 1950; C. A. 44: P7343.

(16) Rubinshtein, Vasseberg, and Pribytkova, Izvest.
     Akad. Nauk S. S. S. R., Otdel. Khim. Nauk 1952,
     323-33; C. A. 46: 9961.

(17)   Sabatier and Mailhe, Compt. rend., <u>148</u>, 898 (1909).

(18)   Upson and Sands, J. Am. Chem. Soc., <u>44</u>, 2306 (1922).

BIOGRAPHICAL SKETCH

David Stanley Cobbledick was born in Huntington,
West Virginia, on August 31, 1929. He attended elementary
and secondary school in Huntington, West Virginia. After
graduation from high school in June, 1947, he enrolled in
Hampden-Sydney College at Hampden-Sydney, Virginia, where
he received the degree of Bachelor of Science in June, 1951.
Graduate work for a Master of Science degree in Chemistry
was completed at Marshall College in Huntington, West
Virginia, in August, 1953.

In September, 1953, Mr. Cobbledick entered the
Graduate School of the University of Florida and served
as a graduate assistant for the Department of Chemistry
from September, 1953, to June, 1955. Since June, 1955,
he has served as a research assistant on a project sup-
ported by the Research Corporation.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

January 26, 1957

C. J. Byers
Dean, College of Arts and Sciences

Dean, Graduate School

SUPERVISORY COMMITTEE:

Chairman

John F. Baxter

Charles B. Smith

100